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# NIST Reactor: Summary of Activities July 1990 Through June 1991



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# **NIST Reactor: Summary of Activities July 1990 Through June 1991**

C. O'Connor, Editor

Reactor Radiation Division  
Materials Science and Engineering Laboratory  
National Institute of Standards and Technology  
Gaithersburg, MD 20899

January 1992



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## FOREWORD

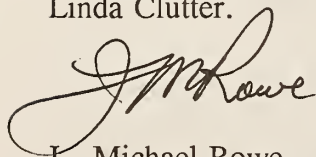
This has been a year of steady progress in the Reactor Radiation Division (RRD), with a reactor availability of better than 90% of scheduled time. Although operating power had to be reduced to 15 MW in April because of repeated problems with one main heat exchanger, the productivity of the facility was high, as can be seen from the number of reports in this summary. New replacement heat exchangers have been ordered, and are now being fabricated, with delivery scheduled for 1992. This year also marks the first use of a fifth generation of fuel element for the NIST reactor, which will improve fuel utilization beyond its already high level.

The dominant feature of the program of research supported by the reactor is the great breadth and diversity of the effort, from measurements of fundamental properties of the neutron to condensed matter physics to polymers to art history and restoration to neutron standards. This year, we have attempted to group contributions into broad general classes, but as is common with such schemes, there remain many ambiguities. We hope that the change is productive, in spite of the somewhat arbitrary nature of the subdivisions. In fact, the very diversity that is the highlight and strength of the program renders it somewhat hard to assign to categories. Out of a multitude of possibilities, however, the following examples will perhaps serve to highlight various areas. Work on the fundamental properties of oxide superconductors continues to provide new insights into these important materials, which offer a rich variety of magnetic and structural phenomena. In particular, the studies of magnetic and atomic dynamics is essential to clarification of the mechanisms that lead to high  $T_c$ . Studies of magnetic multilayers, including new work in magnetic semiconductors which provide a broad range of new phenomena, continues at a high level. Neutron studies of  $C_{60}$  (Buckminsterfullerene) have shown definitively that the disorder in the high temperature phase is due to rotational diffusion, and have also shown that there is residual disorder in the low temperature orientationally ordered phase. The studies of hydrogen in Nb-V alloys have revealed the occupation of octahedral sites, with the lowest excitation energy ever measured in any metal hydride. The availability of the 30-m SANS has allowed new studies of "superanomalous" flow in liquids under shear, and systematic studies of the effects of other process variables. The use of neutron reflectivity as a probe of surfaces and interfaces continues to grow, with increasing sophistication of analysis and technique. The effort to develop maximum entropy methods as an essential tool in biological crystallography has been successfully completed, with computer programs for application of the method developed and running. Finally, a new research collaboration in neutron scattering with the Johns Hopkins University was successfully initiated.

The Cold Neutron Project continues to progress well. The 30-m NIST/Exxon/U. Minn SANS was dedicated in May 1991, and the performance continues to be improved as the inevitable problems are corrected. The neutron lifetime measurements are under way with calibration of the flux measurement systems (both foil and calorimeter) now being established. The analytical chemistry instruments are on line (depth profiling and prompt gamma), and a station to develop neutron focusing methods being used to characterize components and try out concepts. The Center for High Resolution Neutron Scattering (CHRNS) SANS (funded by NSF) is being assembled, and NG-3, which will serve it, is being installed, with completion scheduled for February 1992. Other instruments are in various stages of construction and design, and the supermirror technology is sufficiently developed to allow an order to be placed for guides 1, 2, and 4. As a result of Monte Carlo modeling, a new hydrogen source geometry has been selected which promises a 50% improvement in flux; as a result, detailed design is delayed, while analytical and experimental studies of the new design are being performed at NIST, Boulder. We have initiated the user program at the Cold Neutron Research Facility (CNRF) with a call for proposals, and the response has been quite satisfactory. The proposals are now out for review.

The non-RRD programs at the reactor, both CNRF and thermal neutron, continue to be healthy and productive, and a new program centered in the Polymer Division is now in operation at the 8-m SANS in the guide hall.

In closing, I want again to recognize the dedication and professionalism of the entire staff associated with the reactor—both from within RRD and outside. It gives me great pleasure to congratulate Ted Prince and Tawfik Raby on their receipt of the Department of Commerce Gold Medal for outstanding service to the Nation, and I am sure that they would both want me to add that the work for which they are recognized would not have been possible without the efforts of everyone in the Division. A special word of thanks is due once again to Carol O'Connor for her work on this report. She was ably assisted by Lisa Poole and Linda Clutter.

A handwritten signature in dark ink, appearing to read "J. Michael Rowe". The signature is fluid and cursive, with a large, sweeping initial "J" and "M".

J. Michael Rowe  
Chief, Reactor Radiation Division  
January 1992

## **ABSTRACT**

This report summarizes all the programs which use the NIST reactor. It covers the period for July 1990 through June 1991. The programs range from the use of neutron beams to study the structure and dynamics of materials through nuclear physics and neutron standards to sample irradiations for activation analysis, isotope production, neutron radiography, and nondestructive evaluation.

**KEY WORDS:**        activation analysis; cold neutrons; crystal structure; diffraction;  
                         isotopes; molecular dynamics; neutron; neutron radiography;  
                         nondestructive evaluation; nuclear reactor; radiation.

## **DISCLAIMER**

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## A. CONDENSED MATTER PHYSICS AND THEORY

A great deal of the work in this area is related to studies of oxide superconductors, with a threefold emphasis—structure studies, magnetic properties, and, to a lesser extent, dynamics and mechanisms of superconductivity. This work has benefited from a strong interaction with the superconductivity center at the University of Maryland and from collaborative studies with Brookhaven, MIT, AT&T Bell Laboratories, and DuPont. Our efforts to improve methods to quantitatively determine impurity phases in oxide superconductors provides a necessary tool for characterization of these materials.

Other programs in magnetic semiconductors (with the University of Notre Dame), layered

materials (with the University of Illinois), and structural phase transitions continue to contribute to the effort in condensed matter physics. The experiment on the dynamics of liquid helium in restricted geometries (with the University of Pennsylvania) represents a new departure with interesting results.

The development of new theoretical models for surface roughness and the extensions of an earlier model for bicontinuous structures to fractal structures represents an important step in our understanding of a class of phenomena that are of increasing interest (see reports on reflectivity elsewhere in this report).

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## CRYSTALLOGRAPHIC AND MAGNETIC STRUCTURE OF $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.8}$

J. K. Stalick and J. A. Gotaas

and

S. F. Cheng, J. Cullen, and A. E. Clark (Naval Surface Warfare Center, Silver Spring, MD)

There has been recent interest in the use of nitrided rare earth-iron compounds of the type  $\text{R}_2\text{Fe}_{17}\text{N}_{3-8}$  as permanent magnets. Coey and coworkers [1-3] and Buschow et al. [4] have reported that treatment of  $\text{R}_2\text{Fe}_{17}$  compounds with nitrogen results in a volume expansion of about 7% along with a significant increase in Curie temperature and room temperature magnetization. All compounds exhibit easy-plane anisotropy at room temperature, while retaining the original  $\text{Th}_2\text{Ni}_{17}$  or  $\text{Th}_2\text{Zn}_{17}$  structure type, except for samarium, which is easy-axis [1,2].  $\text{Pr}_2\text{Fe}_{17}$  is highly magnetostrictive at low temperatures; it is plausible to think that raising the Curie temperature by nitrogeation will result in a compound with a large room-temperature magnetostriction. This, taken together with the easy-plane magnetic anisotropy, could make  $\text{Pr}_2\text{Fe}_{17}\text{N}_x$  compounds very attractive transducer materials. We have thus undertaken the structural analysis of  $\text{Pr}_2\text{Fe}_{17}\text{N}_{3-8}$  to determine the position of the interstitial nitrogen for this structure type as well as the magnetic structure of the Pr-containing material.

Alloys of composition  $\text{Pr}_2\text{Fe}_{17}$  were nitrided at 793 K using flowing nitrogen gas. Thermal magnetic measurements showed a change of Curie temperature from 285 K for  $\text{Pr}_2\text{Fe}_{17}$  to 715 K for the nitrided material. Neutron diffraction data were obtained on the NIST high-resolution powder diffractometer at room temperature and at 4 K, and the structure was refined using the Rietveld method. The N atom was placed in the 9e site as suggested by the structure determination of  $\text{Nd}_2\text{Fe}_{17}\text{C}_{0.5}$  by Helmholdt and Buschow [5]. The occupancy of the N atom was refined, along with the occupancies of potential N atoms in the 3a position as suggested by Luo et al. [6,7] and in the 18h position ( $x = 0.115$ ,  $z = 0.05$ ) as suggested by Stadelmaier et al. [8] for similar carbides, as well as in the 18g site reported by Jaswal et al. for  $\text{Nd}_2\text{Fe}_{17}\text{N}_x$  [9]. The regions of scattering of the impurity phase  $\alpha\text{-Fe}$  were excluded from the refinements.

The structure was found to be the expected  $\text{Th}_2\text{Zn}_{17}$  structure type, space group  $R\bar{3}m$ , with  $a = 8.776(1) \text{ \AA}$ ,  $c = 12.649(2) \text{ \AA}$  at 4 K and  $a = 8.794(1) \text{ \AA}$ ,  $c = 12.668(2) \text{ \AA}$  at 295 K. The

N atom was found to occupy the interstitial 9e site, while the occupancies of the alternative 3a, 18h, and 18g sites refined to zero. The occupancy of the 9e site at 4 K is 8.4(1) yielding a composition of  $\text{Pr}_2\text{Fe}_{17}\text{N}_{2.8}$  for this sample, close to the ideal composition  $\text{Pr}_2\text{Fe}_{17}\text{N}_3$  if the 9e site is fully occupied. This confirms the results of Coey et al. [3], who deduced the nitrogen position in  $\text{Sm}_2\text{Fe}_{17}\text{N}_2$  from EXAFS data. The nitrogen atom is octahedrally coordinated by two Pr and four Fe atoms; the Pr-N distance of 2.542(1) Å and the Pr-Fe distances of 1.912(1) Å and 1.934(2) Å at 295 K are consistent with the sums of the covalent radii. The alternative sites for the N atom that have been suggested would result in Fe-N distances of 1.21 - 1.49 Å, considerably shorter than the sum of the radii of N (0.70 Å) and Fe (1.24 Å).

The magnetic moments of the Pr and Fe atoms are ferromagnetically aligned perpendicular to the *c*-axis. The magnetic moment of 3.4(1) $\mu_B$  for Pr at 4 K is close to the free ion moment of 3.2 $\mu_B$ , although the actual moment should be determined by the crystal field anisotropy in the system. At room temperature, the reduced moment of 1.9(1) $\mu_B$  is the result of

thermal disorder. The refined magnetic moments of the Fe atoms range from 2.1(2) - 2.9(2) $\mu_B$  at 4 K and from 2.4(2) - 3.1(1) $\mu_B$  at 295 K. They agree within the standard deviations reported with those found for  $\text{Nd}_2\text{Fe}_{17}\text{C}_{0.5}$  by Helmholdt and Buschow [5], and are close to the typical value of 2.2 $\mu_B$  for Fe.

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## TEMPERATURE DEPENDENCE OF MAGNETIC ORDER IN UPdSn and UPtGe

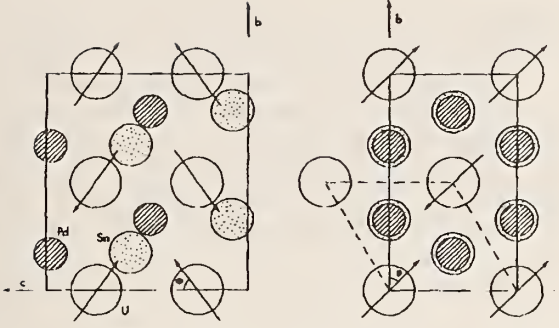
R. A. Robinson and A. C. Lawson (Los Alamos National Laboratory, Los Alamos, NM)  
J. W. Lynn (University of Maryland, College Park, MD and Reactor Radiation Division)  
and

K.H.J. Buschow (Philips Research Laboratories, Eindhoven, The Netherlands)

The intermetallic compounds UPdSn and UPtGe have been studied by means of neutron diffraction. Both materials had been studied previously at LANSCE [1,2] and the intent of the NIST work was to study the temperature dependence of magnetic order in more detail.

UPdSn is one of the set of ternary (1:1:1) uranium-based compounds and crystallizes in the space group  $P6_3mc$  with the hexagonal GaGeLi structure, which is an ordered form of the  $\text{CaIn}_2$  structure type. At low temperature it exhibits the noncollinear antiferromagnetic structure shown in figure 1, with a uranium moment of

2.05  $\pm$  0.13  $\mu_B$ , and where the canting angle  $\phi = 54^\circ$  and  $\theta = 45^\circ$ . Susceptibility measurements indicated that there might be two transitions, the Néel point at  $\approx 40$  K and a second transition at  $\approx 25$  K. The previous neutron measurements showed very different diffraction patterns above and below 25 K, and we thought the intermediate phase might be a simpler structure in which  $\theta = 0$ . This would be indicated by the absence of the (010) reflection, which is the strongest at low temperature. However, the (010) reflection did seem to be present, but only just, above 25 K. To resolve



**Figure 1.** The magnetic structure of UPdSn. The right-hand panel shows the projection onto the orthorhombic  $a,b$  plane, which is the same as the hexagonal basal plane. The hexagonal cell is shown by the dashed lines. The left-hand panel shows a projection onto the orthorhombic  $b,c$  plane. The angle  $\phi$  is  $\approx 54^\circ$  and at the lowest temperature, the angle  $\theta$  is  $\approx 45^\circ$ . The atoms are plotted with half their respective atomic radii; in order of increasing radius, they are Pd, Sn and U.

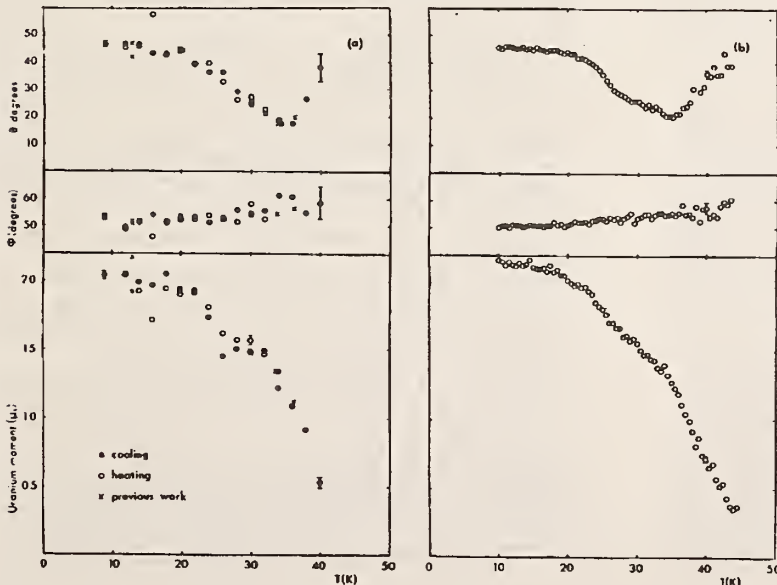
whether this remnant was due to temperature hysteresis, and to clarify the nature of the magnetic phase transitions, we undertook a careful temperature-dependent study.

The results, in terms of the three model parameters,  $\mu$ ,  $\phi$  and  $\theta$ , are shown in figure 2. We show results extracted from integrated intensities, taken both in cooling and heating, in panel (a), while in panel (b) we show similar results extracted from measurements of peak intensities. The statistical precision of the latter results is much greater, but the measurement is more susceptible to systematic errors associated

with background subtraction and possible variation in linewidth, so the results in panel (a) are more reliable for absolute values of the model parameters. We can make the following conclusions: first, there is no temperature hysteresis; second, there is excellent agreement with the LANSCE results; third, there are no sharp transitions below the Néel point and the model parameters vary continuously. Indeed the moment behaves quite normally and  $\phi$  is almost temperature-independent.  $\theta$  does indeed rotate towards the  $b$ - $c$  plane progressively, but at 35 K it appears to move back again.

It is now quite a puzzle to correlate our results with the two peaks in the susceptibility. In addition, the anomalous rotation near the Néel point is also very strange: it may be that we are including critical scattering in our measurement, and as the canting angles become ill-determined there the results are unreliable. We now plan a single crystal experiment to resolve these questions.

As for UPtGe, it is orthorhombic with the NiSiTi structure, and orders magnetically at 52 K. We had previously shown that it exhibited incommensurate magnetic order with  $q = (0, 0.555, 0)$ . In our present work at NIST, we have shown that this  $q$ -vector does not change with temperature and that there is a single order parameter, the uranium moment. Figure 3 shows the variation with temperature of the  $000 \pm$  magnetic reflection.



**Figure 2.** The variation of model parameters for UPdSn, uranium moment,  $\theta$  and  $\phi$ , with temperature as extracted (a) from integrated intensities and (b) from peak intensities. The solid circles represent data taken on cooling while the open circles represent data taken on heating. The crosses represent the data reported in ref. 1.

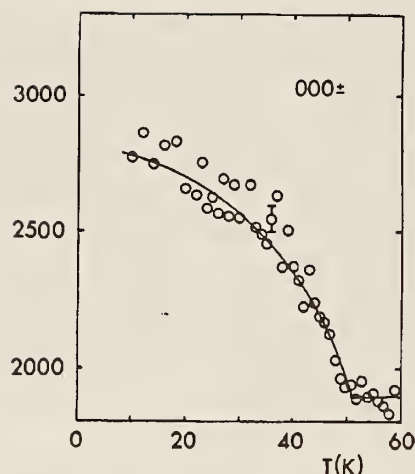


Figure 3. The variation of intensity in the 000  $\pm$  magnetic reflection in UPtGe, with temperature. The line is merely a guide to the eye.

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## ANTIFERROMAGNETIC ORDERING OF $[(\text{CD}_3)_3\text{ND}]\text{FeCl}_3 \cdot 2\text{D}_2\text{O}$ , A ONE-DIMENSIONAL ISING FERROMAGNET

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Recently much attention has been focused on synthesizing organic-based magnets with various desirable properties [1]. Initially, this work focussed on tailoring magnets to have reduced magnetic exchange along one or two dimensions [2]. The series of compounds  $[(\text{CH}_3)_3\text{NH}]\text{MX}_3 \cdot 2\text{H}_2\text{O}$ , where  $\text{X} = \text{Cl}$  or  $\text{Br}$  and  $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni},$  or  $\text{Cu}$  (referred to as MTAX) is characterized by 1-d anisotropic Heisenberg-magnetic behavior. All of the MTAX compounds, with the exception of MnTAB and CuTAC, are orthorhombic, of space group  $Pnma$ . The transition metal ions are at the center of distorted octahedra of four chlorines and two oxygens, with the  $\text{Cl}^-$  ions bridging the  $\text{M}^{2+}$  ions into chains along the  $b$  axis, and the waters of hydration providing  $c$  axis hydrogen bonding of the chains into planes. The large trimethylammonium groups isolate the planes along the  $a$  axis. The title compound,  $[(\text{CH}_3)_3\text{NH}]\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ , FeTAC, is a good example of a 1-d Ising ferromagnet. Susceptibility

measurements [3] indicate the ferromagnetic in trachain exchange is  $J_b/k_B = 17.7$  K and that the small total interchain exchange is antiferromagnetic,  $J'/J_b \approx -0.0013$ . Just above the Néel temperature,  $T_N$ , the easy ( $b$ ) axis susceptibility is a factor of  $10^4$  greater than the  $a$  or  $c$  axis susceptibilities.

Approximately 3.5 g of powdered, fully-deuterated FeTAC were placed in a flat-plate holder in a pumped  $^3\text{He}$  cryostat at BT-9. Figure 1 shows the diffraction pattern at 10 K and the difference between scans at  $T = 0.4$  K and 10 K, over the range  $2^\circ \leq 2\theta \leq 62^\circ$ . The difference pattern indicates the development of long-range magnetic order, which is confirmed by the temperature dependence of the  $2\theta = 8.1^\circ$  peak (fig. 2). The ordering is extremely sharp and suggests that the transition is low-dimensional in nature. For  $T < 2.95$  K, the temperature dependence of the order parameter is well represented by the exact Onsager solution for an anisotropic 2-d Ising lattice, where [4]

$$\frac{M(T)}{M(O)} = \{1 - \sinh^{-2}(J/k_B T) \sinh^{-2}(J'/k_B T)\}^{1/8}$$

and  $J$  and  $J'$  are the two in-plane magnetic exchange constants. In the present case, we have chosen a ratio  $|J'/J| = 1.3 \times 10^{-3}$ . This fit gives a value of  $T_N = 3.02$  K, in close agreement with  $T_N = 3.06$  K determined by dc magnetization measurements of the deuterated compound. A fit to the square 2-d Ising magnetization gives  $T_N = 3.13$  K and an intensity curve which is not as sharp as the data. Given the large difference in the intra- and inter-chain exchange, we expect that the anisotropic 2-d Ising result will be more consistent with the data far from  $T_N$ . The rounding of the observed order parameter in the vicinity of  $T_N$  is probably

due to the inclusion of critical fluctuations in the scattering from a powder; this should be greatly improved by planned single crystal measurements of the Bragg peak intensity.

The observed pattern of magnetic diffraction peaks suggest that the spin configuration is ferromagnetic along the  $b$  axis and staggered along the  $[101]$  direction. A collinear structure accounts for most of the observed magnetic peaks, with the exception of the peak at  $2\theta = 20.42(3)^\circ$ . This extra peak suggests that there is canting in the magnetic structure, in agreement with conclusions based on susceptibility and Mössbauer measurements [3]. Further analysis and single crystal measurements are planned to determine the nature of the canting.

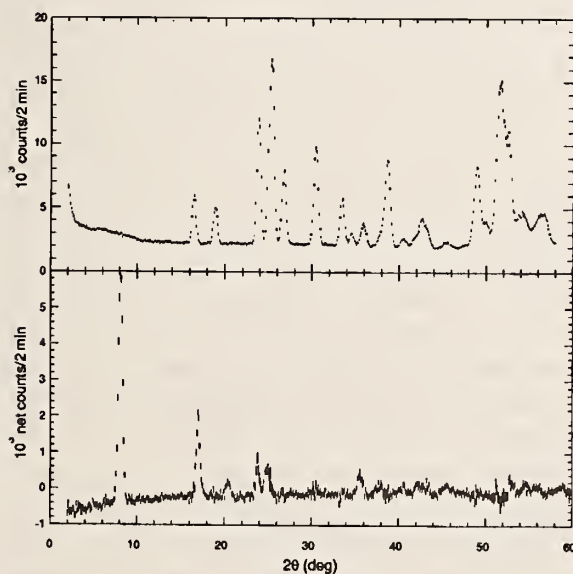


Figure 1. (top)  $2\theta$  scan of FeTAC powder at  $T = 10$  K with  $\lambda = 2.3775$  Å neutrons. (bottom) Difference between  $2\theta$  scans at  $T = 0.4$  K and 10 K.

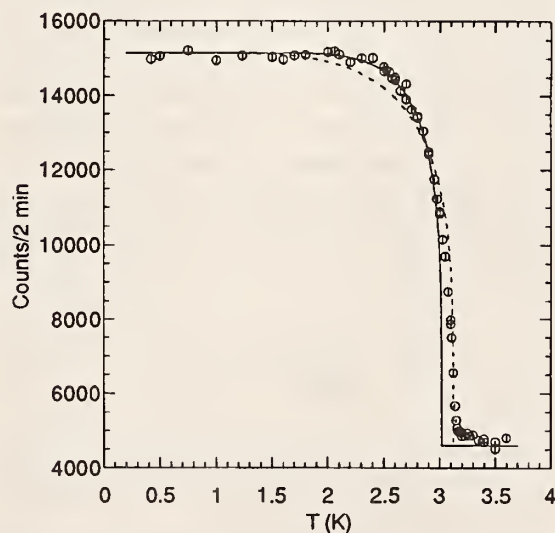


Figure 2. Temperature dependence of the  $2\theta = 8.1(1)^\circ$  peak intensity, indicating  $T_N = 3.16(2)$  K. The solid line is the exact Onsager solution for the magnetization of an anisotropic 2-d Ising lattice with  $J/k_B = 10.2$  K and  $J'/J = 1.3 \times 10^{-3}$ , as described in the text. The dotted line is the exact Onsager solution for a square 2-d Ising lattice.

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# POLARIZATION ANALYSIS OF THE MAGNETIC EXCITATIONS IN INVAR Fe<sub>86</sub>B<sub>14</sub>

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The spin dynamics of isotropic ferromagnets at modest temperatures is known to be well described by linear spin wave theory. In the long wavelength hydrodynamic limit there is a Goldstone mode with dispersion relation given by the familiar expression  $E_{sw} = D(T)q^2$ . The quantitative value of the "stiffness" constant  $D$  depends on the details of the interactions and the nature of the magnetism, such as whether the magnetic electrons are localized or itinerant, or the structure is amorphous or crystalline, but the general form of the spin wave dispersion relation, and hence the spin wave density of states, is invariant. The leading order temperature dependence to the magnetization is then given by  $M(T) = M(0) [1 - B T^{3/2}]$ , where the coefficient  $B$  is related to the spin wave dispersion relation by

$$B = \frac{\zeta(3/2)g\mu_B}{M(0)} \left[ \frac{k_B}{4\pi D} \right]^{3/2}. \quad (2)$$

A measurement of the spin wave dispersion relation can then be directly related to the bulk magnetization, and vice versa.

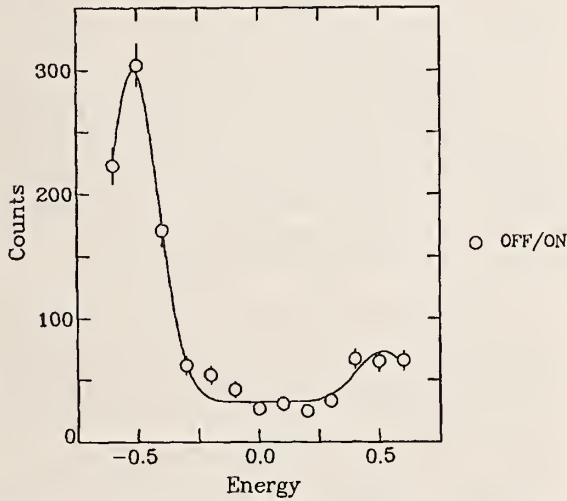
These relationships have been found to be in excellent accord with experimental observations for the vast majority of isotropic ferromagnetic materials, with the singular exception of Invar systems [1,2]. In all the Invar materials, whether they be amorphous or crystalline, eq. (1) is found to fail in a major way, with the observed stiffness constant as much as a factor of two larger than inferred from magnetization measurements. In an attempt to understand the origin of this discrepancy, we previously carried out extensive unpolarized neutron measurements on the amorphous Invar Fe-B system in order to make a detailed comparison between spin wave theory and experiment [2]. We found that spin

wave theory worked remarkably well in describing the long wavelength spin dynamics of this Invar alloy system.

The conventional explanation for the observed behavior is that there are additional "hidden" excitations which participate in reducing the magnetization. The magnetization and neutron measurements already put stringent conditions on the form that such excitations might take, since there is no freedom to change the form of the theory, *viz* the  $T^{3/2}$  behavior for the magnetization, the  $T^{5/2}$  behavior for  $D(T)$ , etc. Hence we must have a density of "hidden" excitations which has precisely the same form as the conventional spin wave excitations themselves. One possibility which has been suggested [3] is that the (transverse) spin wave excitations couple to the longitudinal fluctuations, yielding propagating longitudinal excitations which peak at the transverse spin wave energies. Thus in an unpolarized beam experiment they appear together, and cannot be separated. We have been carrying out inelastic polarized neutron measurements on the Fe<sub>86</sub>B<sub>14</sub> Invar system to explicitly separate the longitudinal spin fluctuation spectrum ( $S^z S^z$ ) from the usual spin wave excitations represented by  $S^\pm = S^x \pm iS^y$ . The measurements reveal the presence of longitudinal excitations, not only in the vicinity of  $T_C$ , but substantially below the ordering temperature as well.

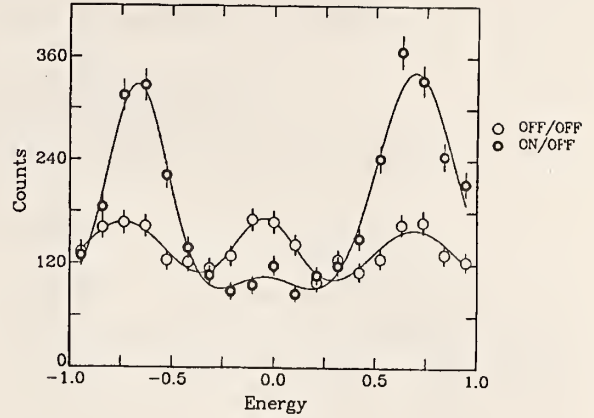
Due to the amorphous nature of the sample, all the present data have been taken in the small wave vector regime, where the spin waves are well defined at low temperatures. The Curie temperature is 556 K, and the low  $T$  spin stiffness coefficient is  $\sim 120 \text{ meV-Å}^2$  [2]. The polarization analysis technique as applied to this problem is in principle straightforward. All the transverse spin wave scattering causes a reversal

of the neutron spin. These spin-flip cross sections are denoted by  $(+-)$  and  $(-+)$ . If the neutron polarization  $\hat{P}$  is parallel to the momentum transfer  $\vec{Q}$ ,  $\hat{P} \parallel \vec{Q}$ , then we may create a spin wave in the  $(-+)$  configuration, or destroy a spin wave in the  $(+-)$  configuration. Longitudinal fluctuations, on the other hand, are invisible in this situation. Figure 1 shows a measurement with the  $(+-)$  configuration. The strong peak on the energy gain side ( $E < 0$ ) corresponds to the destruction of spin wave excitations. The weak peak on the energy loss side ( $E > 0$ ) is caused by the imperfect polarization of the instrument, and the fact that  $\hat{P}$  and  $\vec{Q}$  were not precisely parallel.



**Figure 1.** The  $(+-)$  spin-flip scattering cross section observed at 295 K and  $q = 0.06 \text{ \AA}^{-1}$ . The energy gain side shows a strong spin wave excitation.

In the configuration where  $\hat{P} \perp \vec{Q}$ , the spin wave scattering still causes a neutron spin-flip, but it shows up with equal intensity in the energy gain and energy loss cross section. The non-spin-flip  $(++)$  or  $(--)$  scattering, on the other hand, is directly related to the longitudinal ( $S^z S^z$ ) scattering. Figure 2 shows a measurement in this vertical field configuration. The spin-flip scattering clearly shows spin waves in energy gain and energy loss, as expected, while the non-spin-flip data also display peaks at the spin wave energies. The scattering at the spin wave positions is  $\sim 1/3$  the strength of the spin-flip scattering, while the flipping ratio is  $\sim 10$ . We make the following remarks about this nonspin-



**Figure 2.** Observed scattering in the vertical field configuration ( $\hat{P} \perp \vec{Q}$ ). The spin-flip scattering exhibits the usual spin wave excitations, while the non-spin-flip scattering also reveals excitations near the spin wave energies.

flip scattering: 1) The peak in energy obeys a  $q^2$  dependence. 2) The ratio of the intensity of the spin-flip to nonspin-flip scattering did not change when experimental improvements doubled the flipping ratio. 3) The ratio did not change significantly as a function of  $q$ , while the resolution effects change substantially.

These data strongly suggest that there are longitudinal propagating excitations in this Invar system. These are just the type of excitations which would be needed to explain the "Invar anomaly". However, a word of caution is in order, as the longitudinal and transverse excitation energies are very close to each other, and this is the most likely situation under which "spurious" longitudinal scattering might be found. Therefore, further experimentation is warranted before unambiguous conclusions can be drawn.

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## MAGNETOELASTIC EFFECTS IN Er/Lu THIN FILMS

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In an earlier study of erbium thin films grown epitaxially on nonmagnetic yttrium baselayers [1], it was found that the ferromagnetic phase, which develops in bulk Er below 20 K, is completely suppressed. Its absence was explained by a model for the magnetoelastic energy in which the Er basal plane is stretched toward the Y lattice through elastic coupling of the two elements. This effect inhibits both the basal plane contraction and c-axis expansion that accompany the first-order ferromagnetic transition in bulk Er and shifts the energy balance away from ferromagnetism. As a test of the model, we have studied a series of Er films (400 Å - 9500 Å) [2] grown epitaxially on Lu baselayers which should induce compression of the Er basal plane.

Magnetic neutron scattering experiments performed on a triple axis spectrometer show that all of the Lu based films exhibit magnetic phases similar to bulk erbium. Specifically, the paramagnetic phase of elemental Er gives way at 85 K to one in which the moments order sinusoidally along the c axis with a period near  $T_C$ . At 54 K a helical spin component develops in the basal plane and the c-axis modulation (CAM) begins to square up. At 20 K the competition between the exchange and magnetoelastic energies drives a first-order transition to a cone state, ferromagnetic along the c axis while remaining helical in the basal plane.

For the Er/Lu films the CAM wavevector was extracted from the positions of the magnetic satellites of the (1010) reflection. The resulting phase angle falls up to 3° below the bulk values. This behavior contrasts with turn angles for Er/Y films, [3] which are as much as 2.5° per layer larger than bulk. In figure 1 the 30 K phase angle data plotted as a function of Er thickness demonstrate that the CAM periodicity approaches bulk behavior as the film thickness is increased.

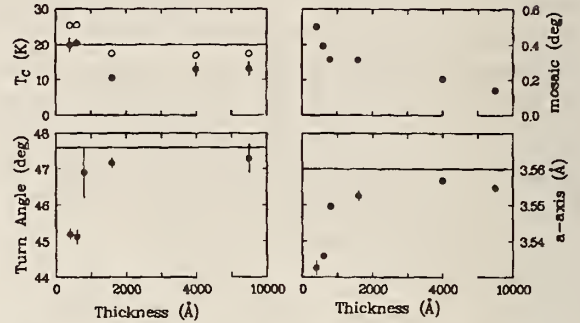


Figure 1. Er thickness dependence of the phase angle of the c-axis modulated spin structure at 30 K along with the Curie temperature upon heating (open circles) and cooling (shaded circles). Also plotted are the a-axis lattice parameter and out-of-plane mosaic of the Er/Lu films. The solid lines mark the corresponding bulk values.

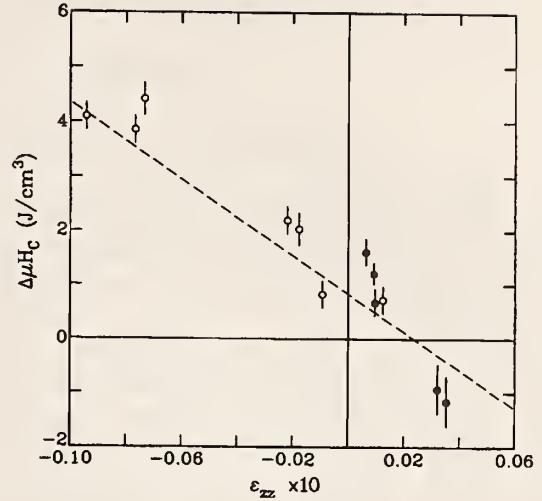
Contrasting with the Er/Y films, the CAM collapses to a conical ferromagnet near 20 K in all of the Lu based films except for one 800 Å thick. The plot of the transition temperature versus film thickness in figure 1 shows that  $T_C$  is enhanced from the 20 K Er value for the 400 Å and 600 Å films and reduced from bulk for thicker films. In addition the hysteresis through the transition ranges from 5 K to 10 K relative to the 1.5 K hysteresis observed in elemental Er [4].

Structural characteristics of the films obtained by x-ray diffraction techniques correlate strongly with the magnetic properties. The a-axis spacing of the Er layer at room temperature is plotted as a function of Er layer thickness in figure 1. For films thinner than 800 Å, the lattice parameter approaches, but does not equal, the smaller Lu value; the Er and Lu lattices are not coherent in the growth plane. The erbium layer relaxes sharply with increasing film thickness, as expected. The slope of approach changes near 800 Å coinciding with the cross-over in the Curie temperature and turn angle data. Similar to the yttrium based films [1], bulk Er spacings are not fully recovered for even the thickest 9500 Å film.

The out-of-plane mosaic determined from the width of rocking curves through the (0002) reflection provides an indirect measure of the density of misfit dislocations. As demonstrated for ErAs films on GaAs substrates [5], an increase of the mosaic generally accompanies strain relief. Instead the room temperature values for the Er/Lu films plotted in figure 1 fall off exponentially with increasing Er thickness to a value near  $0.1^\circ$  for the 9500 Å film. The relaxation of the Er lattice is apparently associated with the dilution or "healing", rather than the formation, of defects.

The properties of the Er/Lu films summarized in figure 1 can clearly be divided into three regions:  $t < 800$  Å,  $t \approx 800$  Å and  $t > 800$  Å. In the first, the lattice is significantly strained by the Lu base layer, the phase angle of the spin order is reduced from bulk and  $T_C$  is enhanced from 20 K. In the second, the lattice is partly relaxed and the ferromagnetic phase is suppressed. In the third region, the strain is relieved and  $T_C$  is slightly reduced from 20 K.

The modified transition temperatures observed in the Er/Lu films are consistent with a magnetoelastic energy model developed to explain the suppression of ferromagnetism in the Er/Y films [1]. Assuming epitaxial growth of the Er on the Lu layer, an elastic energy contribution from the Lu lattice is added to the magnetoelastic energy term for bulk Er. The Er and Lu basal plane lattice parameters are constrained to be equal at the interface, and the total magnetoelastic energy is minimized with respect to strain. The difference between the magnetoelastic energy of the ferromagnetic and antiferromagnetic configurations can then be calculated as a function of the lattice strains and compared to the opposing exchange barrier [6] of  $1.01 \text{ J/cm}^3$ . In figure 2 the driving energy plotted as a function of  $\epsilon_{zz}$  is compared to the energy equivalent of the low temperature critical field or to the difference between the measured and bulk  $T_C$  for the Er/Lu and Er/Y films. Clearly the strain induced by epitaxial growth on the smaller Lu lattice or bigger Y baselayer is responsible for the thickness dependence of the magnetic properties observed in both systems.



**Figure 2.** Magnetoelastic driving energy for the ferromagnetic transition plotted as a function of c-axis strain. The energy was calculated from the model described in the text. Energy equivalents of the low temperature critical fields or the differences between the measured and bulk  $T_C$  upon cooling for the Er/Y films and superlattices [1] (open circles) and Er/Lu films (closed circles) are plotted for comparison.

The effects of epitaxial strain on the magnetic behavior of Er on Y carry smoothly over to the Er/Lu systems where the Er is compressed rather than stretched in the basal plane. The Er/Lu results suggest the introduction of a "cross-over" thickness near 800 Å at which the Er lattice is significantly relaxed. Additional structural characterization is in progress to identify the mechanism responsible for strain relief.

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## POLARIZED NEUTRON GRAZING ANGLE DIFFRACTION

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We have carried out the first measurements employing the grazing-angle diffraction geometry using polarized neutrons and observed the magnetization of an Y/Gd film. Magnetic materials (both films and multilayers) have received a great deal of attention both because of their inherent technological utility and for the richness of behavior they exhibit. A number of experimental techniques, of varying quantitative value, have evolved to observe this behavior (e.g., magneto-optic Kerr effect [MOKE], spin-polarized low-energy electron diffraction [SPLEED], and spin-polarized photoemission). We have for the past several years been exploring the possible uses of grazing-angle neutron diffraction for the study of interfacial problems [1,2]. Neutron diffraction methods possess the advantage that the extraction of quantitative information is straightforward (described by the first Born approximation for most materials).

In grazing-angle diffraction, a finely collimated beam strikes the surface of a flat sample at an angle of incidence near the critical angle for total external reflection. Glancing angles of incidence and exit ensure that the probe intensity is confined to a thin layer at the interface. Weakly interacting waves such as x rays and neutrons can in this way be used to study physics and chemistry at surfaces and interfaces.

Our experiment was performed on the BT-7 reflectometer at NIST [3]. In this instrument, a focussing graphite monochromator produces a monochromatic neutron beam of wavelength  $2.37 \pm 0.02 \text{ \AA}$ , which is collimated by slits to an angular divergence of about 1 arcmin. A unique polarization of the beam is selected by reflection from a ferromagnetic FeSi supermirror. For this experiment we suspended a shielded  $^3\text{He}$  tube above the sample table, used the arc motions of the goniometer head to align the sample in-plane, and manually positioned the detector to specify the diffraction angle. The data were collected as a function of either

incident angle or rocking angle of the goniometer head and integrated over diffracted exit angle. For this experiment, we used a 3-in diam film grown by molecular beam epitaxy, consisting of a  $150 \text{ \AA}$  Y(0001) film atop  $5000 \text{ \AA}$  of Gd and studied the (1120) in-plane Bragg peak. Figure 1 shows a plot of intensity versus incident wavevector  $k_z = (2\pi/\lambda)\sin\phi$ , where  $\phi$  is the angle of incidence of the neutron beam onto the sample with the detector set at  $2\Theta_B = 82^\circ$ . The two spin states exhibit the same intensity at small  $k_z$ , because the neutrons only illuminate the topmost atoms (those in the non-magnetic yttrium layer). As the wavevector increases, the ferromagnetically aligned gadolinium atoms are probed and cause a splitting of the polarization states that falls away at the largest incident angles as the crystal moves away from the Bragg condition.

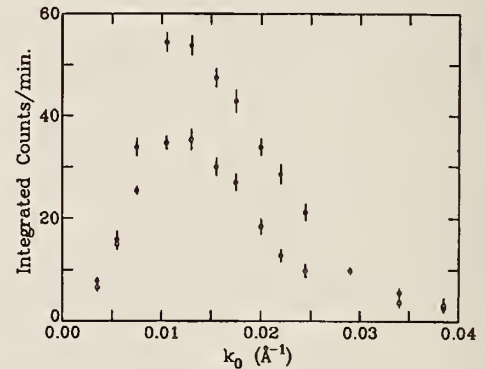


Figure 1. Rod scan of Y/Gd(1120) at  $T = 150 \text{ K}$ .

We have measured diffraction using polarized neutrons in the grazing-angle geometry. The next step in the development of this technique is the extraction of quantitative information from the data. We have outlined a formalism for this data analysis [3,4] and are obtaining a position-sensitive detector capable of resolving the exit diffracted intensity into its wavevector components (an essential requirement for the determination of structural parameters). This improvement in instrumentation coupled

with the theoretical formalism should produce quantitative results in the near future.

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## ANISOTROPIC SPIN COUPLING IN Gd/Y SUPERLATTICES

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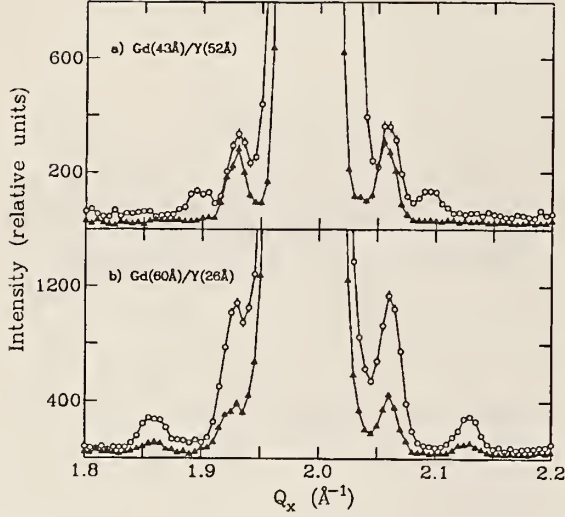
Studies of c-axis rare-earth superlattices such as Gd/Y [1] and Dy/Y [2] have demonstrated that the magnetic order propagates through nonmagnetic interlayers with an interaction strength ranging from 1 to 10 K/magnetic ion. Specifically, for the Gd/Y system the alignment of the ferromagnetic Gd layers fluctuates from ferromagnetic to antiferromagnetic with a period of 25 Å as the yttrium layer thickness is increased. The strength, range and oscillatory nature of this spin coupling is consistent with a simple model describing the indirect RKKY interaction resulting from the polarization of the Y conduction band by the adjacent gadolinium moments [3]. This interaction, however, should decay sharply along the a- and b-axis directions due to anisotropic nesting features in the yttrium Fermi surface [4]. To probe the symmetry of the RKKY coupling mechanism, we have examined three epitaxial b-axis Gd/Y superlattices, b-[Gd<sub>43Å</sub>|Y<sub>52Å</sub>]<sub>85</sub>, b-[Gd<sub>47Å</sub>|Y<sub>42Å</sub>]<sub>50</sub> and b-[Gd<sub>60Å</sub>|Y<sub>26Å</sub>]<sub>80</sub>, by neutron diffraction techniques.

Typical scans along the b\* direction for b-[Gd<sub>43Å</sub>|Y<sub>52Å</sub>]<sub>85</sub>, the sample with the thickest Y interlayer, are shown in figure 1a. The large central peak is the (10 $\bar{1}$ 0) reflection from the yttrium substrate. The 315 K data show distinct superlattice satellites separated from each other

by  $\Delta Q = 2n\pi/\Lambda$  where  $\Lambda \approx 95$  Å is the period of the superlattice. Below T<sub>C</sub>, the presence of magnetic peaks with a periodicity of 2Λ suggests that the Gd layer moments anti-align across the Y interlayers. For contrast, diffraction data for b-[Gd<sub>60Å</sub>|Y<sub>26Å</sub>]<sub>80</sub>, the sample with the thinnest Y interlayer, are shown in figure 1b. The extra intensity evident at the superlattice satellite positions at 90 K indicates that the Gd layer moments are aligned. Antiferromagnetic order develops, however, at temperatures greater than 120 K. At 90 K the third sample, b-[Gd<sub>47Å</sub>|Y<sub>42Å</sub>]<sub>50</sub> exhibits a spin state with mixed ferromagnetic and antiferromagnetic order.

For all three samples the strength of the antiferromagnetic coupling at 150 K is proportional to the c-axis saturation fields which equal 80 G, 35 G and 20 G for b-[Gd<sub>43Å</sub>|Y<sub>52Å</sub>]<sub>85</sub>, b-[Gd<sub>47Å</sub>|Y<sub>42Å</sub>]<sub>50</sub> and, b-[Gd<sub>60Å</sub>|Y<sub>26Å</sub>]<sub>80</sub> respectively. The fields decrease slightly with decreasing Y thickness and are significantly smaller than those measured for c-axis Gd/Y systems (ie.  $\approx 1$  kG) [1].

The reduction of the saturation fields may follow from the anisotropic nature of the RKKY-like exchange interaction. In previous studies of b-axis Dy/Y superlattices [5] it was suggested that the range of the coupling along the b-axis is a factor of 10 less than that along the c-axis. For comparison, we have derived a



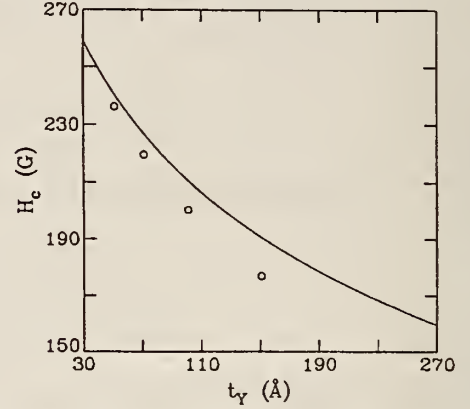
**Figure 1.** a) Neutron diffraction scans along the  $b^*$  direction for  $b\text{-}[\text{Gd}_{43\text{\AA}}|\text{Y}_{52\text{\AA}}]_{85}$  at 80 K (circles) and 315 K (triangles). At 80 K peaks develop with twice the bilayer periodicity indicating that the Gd layer moments are anti-aligned. b) Neutron diffraction scans along the  $b^*$  direction for  $b\text{-}[\text{Gd}_{60\text{\AA}}|\text{Y}_{26\text{\AA}}]_{80}$  at 90 K (circles) and 315 K (triangles). The extra intensity evident at the superlattice satellite positions at 90 K indicates that the Gd layer moments are aligned.

relationship for the strength of the dipolar coupling between two finite ferromagnetic sheets. Because the magnitude of the interaction tends to zero as the width of the slabs approaches infinity, it is only necessary to include contributions from the moments at the ends of each sheet. The resulting expression for the critical field is

$$H_c = 4M \frac{t_{gd}}{W} \ln\left(\frac{W}{t_{Gd} + t_y}\right) \quad (3)$$

where  $M$  is the magnitude of the Gd moment,  $W$  is the width of the Gd slabs and  $t_{Gd}$  and  $t_y$  are the thicknesses of the Gd and Y layers respectively. The strength of the field required to align sheets ( $\approx 4000 \text{\AA} \times 4000 \text{\AA}$ ) is the same order as the measured saturation fields and falls off gradually as the spacing between the sheets is increased as shown in figure 2. For the  $b$ -axis Gd/Y systems we suggest that the exchange coupling, which favors ferromagnet alignment of the Gd sheets, competes with the dipolar coupling which favors antiferromagnetic alignment. In 3-d both the dipolar and the ideal RKKY interaction fall off as  $1/r^3$ . Since the

RKKY interaction depends on conduction electron transport, mean free path effects give rise to damping terms. The range of the dipolar interaction is thus greater than that of the RKKY interaction. A similar effect in lower dimensions may explain why the Gd moments have a tendency to anti-align for thicker Y layers.



**Figure 2.** Applied field required to align two finite ferromagnetic sheets plotted as a function of the separation distance  $t_y$ . The calculation assumes dipolar coupling between sheets  $4000 \text{\AA} \times 4000 \text{\AA}$  with  $t_{Gd} = 29 \text{\AA}$ . The solid line corresponds to the approximation described in the text, and the points were determined by a direct summation technique.

The results for the  $b$ -axis Gd/Y superlattices clearly confirm the asymmetric nature of the RKKY spin interaction. In addition, the spin alignment is apparently determined by a competition between the exchange and dipolar coupling which are of comparable magnitude. Additional samples are being prepared to characterize further the nature of the spin coupling.

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## MAGNETIC PROPERTIES OF Dy/Lu SUPERLATTICES

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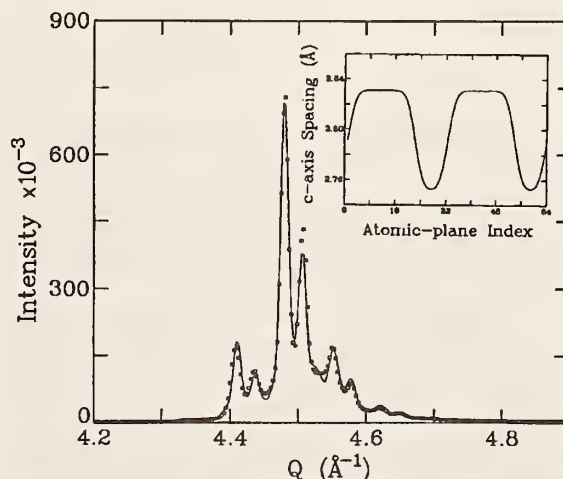
The evolution of molecular beam epitaxy (M.B.E.) has led to the ability to tailor materials on the atomic scale. The one dimensional periodic confinement of alternating materials in a superlattice is the simplest step in that direction. Since the first metallic superlattices were constructed in the early 1980's, a variety of magnetic superlattices including Dy/Y [1], Gd/Y [2] and Fe/Cr [3] have been studied to characterize the origin and nature of spin coupling across nonmagnetic interlayers. As a continuation of this effort, we have probed the structural and magnetic properties of a series of epitaxial dysprosium/lutetium superlattices using neutron and x-ray scattering techniques.

In elemental Dy, at  $T_N = 178$  K ferromagnetic planes perpendicular to the c-axis form a spiral structure; the spins rotate from one sheet to the next by a turn angle of  $43^\circ$ . The phase advance decreases to  $26.5^\circ$  at 85 K, where a spontaneous first order transition to a-axis ferromagnetism is driven by the competition between the exchange and magnetoelastic energies. This is accompanied by a 0.5% orthorhombic distortion of the basal plane.

Previous studies of c-axis Dy/Y superlattices show that the Dy spiral order propagates across the intervening nonmagnetic yttrium [1] via a spin-density wave stabilized in the Y conduction band. In addition, the ferromagnetic phase of Dy is completely suppressed by the epitaxial clamping of the Dy to the nonmagnetostrictive Y layers and substrate. Though the Lu band structure is similar to that of Y, epitaxial strains produced in a superlattice with Dy layers should be quite different. While Dy expands to accommodate the Y atomic spacing, the 1.2% lattice mismatch between Dy and Lu compresses the Dy in the basal plane.

Room temperature x-ray scans along the  $b^*$  direction verify that the Dy and Lu layers are lattice-matched in the basal plane. The coherent

growth gives rise to a periodic strain gradient along the c-axis that can be characterized from fits of the  $(000l)$  scans to a damped rectangle wave model [1]. Using the Hendricks-Teller approximation [4], the model has been modified to include various types of structural disorder [5]. A typical scan and fit are shown in figure 1 for the superlattice  $[\text{Dy}_{21}|\text{Lu}_{10}]_{70}$ . According to the fit this sample consists of an average of 21 planes of Dy and 10 planes of Lu in each bilayer with interfacial diffusion over 4-5 lattice planes. The number of Dy and Lu layers per bilayer vary locally with a full-width of 2 planes and 1 plane respectively. The resulting profile of the c-axis spacings for a single bilayer is shown in the inset.



**Figure 1.** Room temperature x-ray diffraction scan through the  $(0004)$  reflection for  $[\text{Dy}_{21}|\text{Lu}_{10}]_{70}$ . The splitting results from  $\alpha 1$  and  $\alpha 2$  radiation produced by the Cu source. The inset shows the profile of the c-axis lattice parameter through two bilayers obtained from fits of the data to the model described in the text.

Figure 2 shows complementary neutron scans through the  $(0002)$  reflection for  $[\text{Dy}_{15}|\text{Lu}_{15}]_{40}$  at 160 K and 15 K. In addition to the central structural peaks, the 160 K data exhibit the signature of the Dy spiral phase. In fact all five superlattices examined display long range spiral order below  $T_N \approx 175$  K. The helix

in the superlattices advances in the Dy at no more than  $31^\circ$ /layer, with the smallest turn angle of  $26^\circ$  observed at the ferromagnetic transition. The phase angle is smaller at any given temperature than in Dy/Y superlattices or in elemental Dy. The spiral order propagates coherently through the Lu with a phase advance of roughly  $45^\circ$  per Lu layer. This value is close to the maximum in the generalized susceptibility of the nonmagnetic element [6], as is the case in the Dy/Y system.

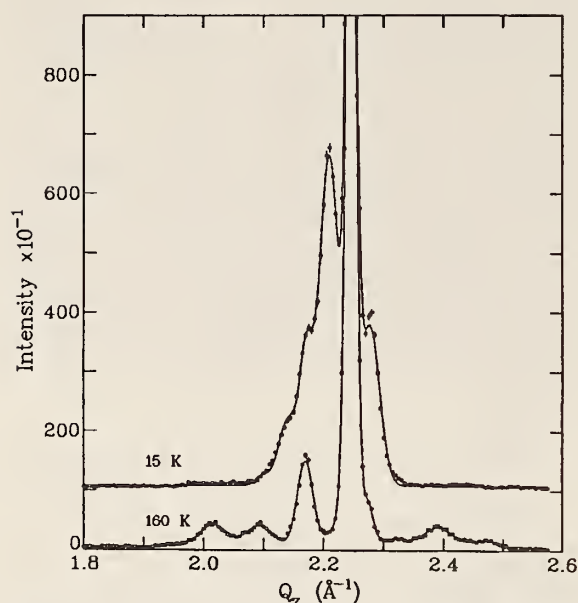


Figure 2. Neutron diffraction scans through the (0002) reflection for  $[\text{Dy}_{15}|\text{Lu}_{15}]_{40}$  at 160 K and 15 K.

In figure 2 the presence of magnetic peaks between the structural superlattice peaks at 15 K corresponds to a doubling of the chemical unit cell; each Dy layer is ferromagnetic, but alternating layers are oppositely aligned across the Lu interlayers. We observe that the three superlattices with the thickest Lu interlayers order with anti-aligned Dy layers at 160 K, 150 K and 145 K for  $[\text{Dy}_{16}|\text{Lu}_{20}]_{60}$ ,  $[\text{Dy}_{15}|\text{Lu}_{15}]_{40}$  and  $[\text{Dy}_{21}|\text{Lu}_{10}]_{70}$ , respectively. In contrast the Dy layer moments in the two samples with the thinnest Lu,  $[\text{Dy}_{14}|\text{Lu}_8]_{70}$  and  $[\text{Dy}_{14}|\text{Lu}_{5.5}]_{80}$ , are ferromagnetically aligned below  $\approx 140$  K. We note that both ferromagnetic and antiferromagnetic interlayer coupling were also evident in c-axis Gd/Y superlattices [2].

In comparison to the bulk Dy value of 85 K,  $T_C$  is enhanced by as much as 80 K. A

model for the magnetoelastic energy [1], which successfully predicted the critical fields for Dy/Y superlattices, was also able to account for the transition temperature as it related to strain in a series of Er films grown on Lu buffer layers [7]. The same model, applied to the Dy/Lu series, does predict a small jump in  $T_C$ .

The model assumes that the Dy layers are highly strained and forced to follow the normal thermal expansion of the Lu interlayers. X-ray data obtained at the NSLS, however, reveal a distortion of the entire superlattice basal plane, approximately 85% of the anomalous strain observed in bulk Dy, accompanying the spiral-ferromagnetic transition. Additional synchrotron and neutron measurements are in progress to correlate changes in the structural and magnetic order through the ferromagnetic transition.

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# NORMAL MODES AND STRUCTURE FACTOR FOR A CANTED SPIN SYSTEM: THE GENERALIZED VILLAIN MODEL

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 and  
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We have studied the generalized Villain model (GVM), which is one of the simplest periodic frustrated systems. Because it is a frustrated spin system, it contains a key ingredient of any model claiming to describe reentrant-spin-glass behavior (RSG), and because it is periodic we can obtain exact solutions of the spin-wave dynamics. This may eventually be useful in separating the effect of randomness from other possible mechanisms for spin-wave damping, such as the coupling of transverse and longitudinal degrees of freedom due to canting. Furthermore, for a certain parameter range, the GVM has a phase transition from a collinear to a canted state. This is of interest because there has been some controversy regarding the extent of the breakup of ferromagnet order in the RSG phase [1-2].

The Villain model (VM) consists of spins on a square lattice, with nearest neighbor interactions. Vertical bonds are all  $J$ , and the horizontal bonds are alternately  $J$  and  $-J$ , according as they lie on even or odd numbered rows. Every square (or plaquette) of spins has a single antiferromagnetic bond, and thus a system of Ising spins is frustrated.

Berge et al. have also defined a generalization of this model, the GVM, in which the  $-J$  bonds take on the values  $J' \equiv -\eta J$ , and for  $J > 0$  the quantity  $\eta$  was varied [3]. We consider, at zero temperature, the normal modes and their structure factor for the GVM, treating three-component spins in the linear spin-wave approximation.

This problem is in the class of models described by the Hamiltonian

$$H = -\frac{1}{2} \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j - \sum_i \vec{S}_i \cdot \vec{H} \quad (1)$$

which consists of an exchange part and a Zeeman part. We assume that the spins have

been equilibrated, and now turn to the question of the spin dynamics.

Linearizing the equations of motion for transverse spin deviation components,  $\alpha_i$  and  $\beta_i$ , defined with respect to the local equilibrium spin direction, one finds eqs. (3.9) of Walstedt and Walker [4]

$$\ddot{\alpha}_i = \lambda_i \beta_i - J_{ij} [(\vec{\beta}_i \cdot \vec{\alpha}_j) \alpha_j + (\vec{\beta}_i \cdot \vec{\beta}_j) \beta_j], \quad (2)$$

$$\ddot{\beta}_i = -\lambda_i \alpha_i + J_{ij} [(\vec{\alpha}_i \cdot \vec{\alpha}_j) \alpha_j + (\vec{\alpha}_i \cdot \vec{\beta}_j) \beta_j]. \quad (3)$$

Note that the relative canting angles appear in the coefficients of these equations. Applying orthonormalization conditions, the structure factors for a given eigenmode can be calculated as,

$$\tilde{S}(\vec{q}) = \left| \sum_i e^{-i\vec{q} \cdot \vec{r}_i} \vec{S}_i \right|^2. \quad (4)$$

As an example of our calculations, the energies and structure factors are shown for  $\eta = 0.5$  in figure 1. Here the frustration is sufficiently strong to produce a canted ground state, with acoustic modes having zero energy at the reciprocal lattice points produced by the canting. Furthermore, there are two acoustic branches, one with ferromagnetic character and one with antiferromagnetic character, since the system has a net magnetization with antiferromagnetic order of the  $x$ -components of the spins. For  $\eta > 1/3$ ,  $(1,0)$  is a magnetic reciprocal lattice point, and as expected the antiferromagnetic branch indeed has a diverging structure factor there. Note that there are several mode crossings which should produce strong mode couplings. Furthermore, there are now two optic branches. We have also shown that the effect of a uniform magnetic field, which produces an excitation gap for the ferromagnetic-like modes, results in strong shifts of the mode crossing points compared to the zero-field case.

While these calculations are interesting as a demonstration of the feasibility of such numerical studies, they also contain insights about the behavior of canted systems. There are two important differences between the spin dynamics of the ferromagnetic and the reentrant-canted phases, which could have been predicted without the above calculations. First, mode softening occurs in the zone boundary region of reciprocal space, since the magnetic unit cell doubles in going from the ferromagnetic ( $\eta < 1/3$ ) to the canted ( $\eta > 1/3$ ) phase. Second, additional nonferromagnetic (AFM) modes appear. Our calculations of the structure factor show that the AFM  $S(q)$  increases linearly from zero at the zone center, and at fixed finite wavevector it increases as the canting angles increase. As expected, the AFM amplitude diverges at the new AFM-like Bragg peaks in the canted state. Such antiferromagnetic modes have long been predicted for spin-glasses and RSG systems on the basis of hydrodynamic arguments [5], although their experimental detection has proved elusive. This is perhaps because for spin-glasses the wave-vector is well-defined as a good "quantum number" only for small  $q$ , and in that regime the structure factor  $S(q)$  is small.

We also conclude that certain qualitative features of the GVM should persist in the randomized canted systems. These features include mode softening near quasi-Bragg peaks at values of momentum transfer corresponding to the next-nearest-neighbor spacings (AFM-like periodicity). These soft modes should have both ferromagnetic and AFM character. In addition optic modes should appear having their largest structure factor near the AFM-like quasi-Bragg peaks. The amplitude of the AFM acoustic mode vanishes as the origin of wave-vector space is approached, whereas its amplitude at finite wave-vectors is correlated with the canting angles. Predictions concerning the behavior of the ferromagnetic acoustic modes at the zone center, must await further theoretical work on the finite temperature dynamics.

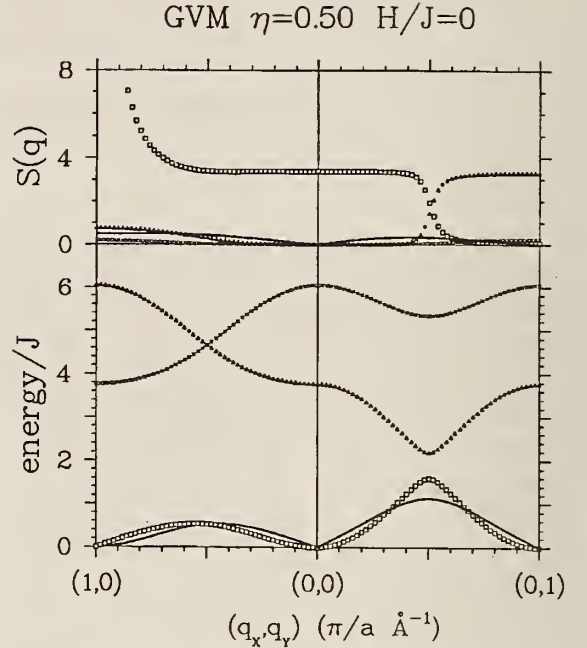


Figure 1. Spin-wave dispersion and structure factor for the generalized Villain model with  $\eta = 0.5$ , which has a canted ferromagnetic ground state. Once the system cants there is an antiferromagnetic mode with infinite structure factor along with a ferromagnetic mode at (1,0). There are also optic modes with finite structure factor near (1,0).

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# STRAIN AND OTHER SYMMETRY BREAKING EFFECTS IN MAGNETIC SEMICONDUCTORS

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Zinc blende (ZB) magnetic semiconductors (MS) provide prototypical systems for study of Heisenberg frustrated antiferromagnets [1]. In the ideal case such systems are Type III antiferromagnets with first order paramagnet-antiferromagnet phase transition [2]. However, if the cubic symmetry is broken (e.g., by a strain field or by dilution of the magnetic sublattice with nonmagnetic ions), the system is expected to form a rich variety of magnetic ground state configurations [3]; at the same time its critical behavior is expected to change from first order to second order transition [4].

The molecular beam epitaxy (MBE) grown magnetic semiconductor systems provide good opportunity for such studies. First, a very large strain can be introduced into the sample by growing heterostructures composed of interleaving layers of materials with different lattice constants. The choice of a larger or smaller lattice constant of the non-magnetic spacers results in achieving either compressive or tensile strain. Secondly, the composition of the samples can be controlled to achieve the magnetic dilution. It has been well established that MBE-grown samples are of good crystalline quality with clean interfaces, and that they are as good models for a magnetism study as the hypothetical bulk-grown samples.

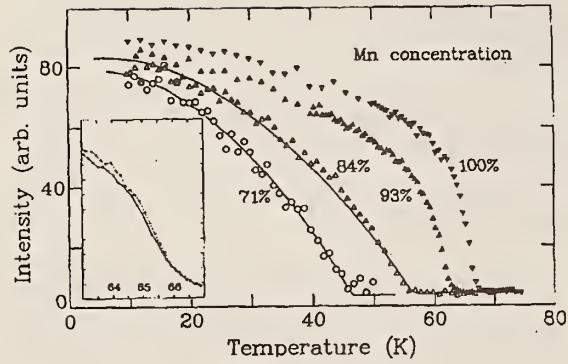
Previous to the work described in this report we investigated ZnSe/MnSe and ZnTe/MnTe superlattices with compressive strain [5]. Since then, we extended our work to ZnTe/MnSe superlattices exhibiting tensile strain and to  $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$  weakly diluted epitaxial layers ( $0.7 \leq x \leq 1$ ). We have confirmed the crossover to the second order magnetic phase transition in all ZnTe/MnSe samples and in  $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$  epilayers for  $x < 0.94$  (fig. 1).

The second order transition is evident in the 71% and 84%  $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$  samples, with Néel temperatures of 46 K and 57 K, respectively. However, in 93% and 100% samples there was a much sharper falloff of the magnetization below the Néel temperature (respectively 62 K and 66 K), indicating the crossover to a first order transition. There is a supporting evidence of that in the magnetization hysteresis observed near the transition point.

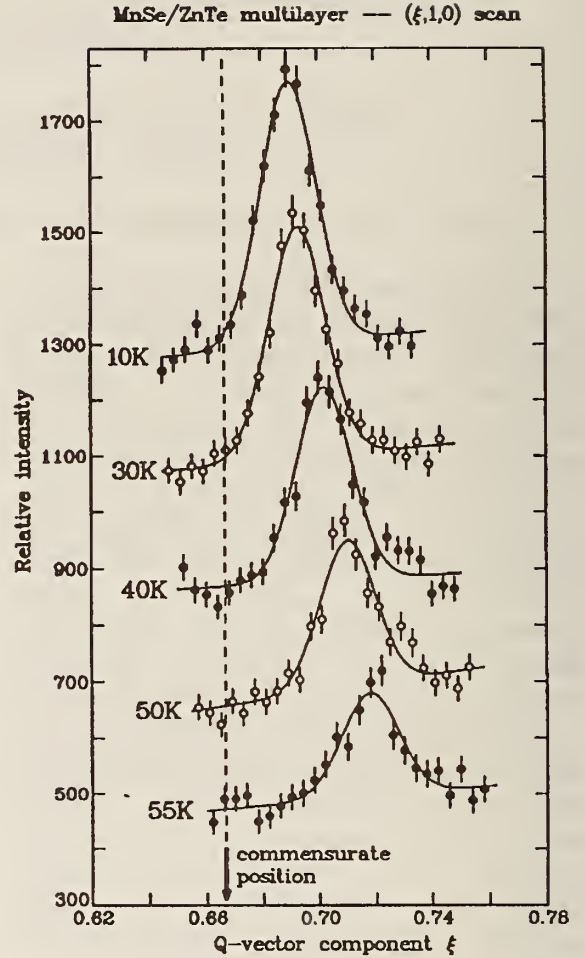
The ZnTe/MnSe superlattices differ from other MS systems by exhibiting an unusual helical AF structure that can be described as a generalization of the Type III fcc AF order seen in unstrained ZB MS systems such as MnSe/ZnSe and MnTe/ZnTe superlattices with compressive strain. This structure has a magnetic cell whose one dimension is incommensurate with the chemical cell dimensions, although it is nearly triple its size (fig. 2).

Such helicoidal structure is favored by the Dzyaloshinskii-Moriya interaction present in the MS systems. However, since there is a considerable strain and strain-induced anisotropy in the nearest-neighbor exchange interaction, we offer a simpler explanation of the origin of this structure, based on the energy analysis of distorted AF bonds [6].

These results show the variety of physical model situations that can be realized in MBE-grown MS systems. We plan to pursue the studies of magnetic phenomena in these samples, and in particular to study the effects of pressure-induced strain. The interface and dimensionality effects will be also investigated.



**Figure 1.** Temperature dependence of the squared sublattice magnetization, as determined from the magnetic scattering intensity. For the lower concentration samples, the transition is of the second order, and it agrees well with the square Brillouin function mean field formula for spin (solid lines). The 93% and 100% concentration samples exhibit different behavior, analogous to the first order transition in  $\beta$ -MnS (ref. [7]). The insert shows the slow (1 K/hr) scan increasing (open circles) and decreasing (dark circles) near the transition temperature in the MnTe sample, showing the magnetization hysteresis (figure adapted from [8]).



**Figure 2.** Examples of  $(\xi, 1, 0)$  diffraction scan data from a MnSe/ZnTe superlattice at various temperatures showing a shift of the magnetic peak from the commensurate  $(\frac{1}{2}, 1, 0)$  position, and the dependence of this shift on  $T$ .

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SMALL-ANGLE NEUTRON SCATTERING OF  
NANODISPERSED MAGNETIC PARTICLES

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Granular magnetic materials, which consist of fine magnetic particles dispersed in an amorphous insulating matrix, display a number of unique properties as a result of their nanometer-scale microstructure [1]. However, many properties of granular magnetic composites are still poorly understood at the fundamental level, such as the exact nature of the magnetic ordering and magnetic excitations within and between the grains. A well known property of single-domain magnetic particles is the occurrence of superparamagnetic relaxation, resulting from the thermally activated fluctuation of the particle moment. Superparamagnetism can be observed on different time scales  $t$  by using different magnetic probes, such as SQUID magnetometry ( $t \approx 10$  sec) and  $^{57}\text{Fe}$  Mössbauer spectroscopy (MS) ( $t \approx 10^{-8}$  sec). In contrast, it may be possible using small-angle neutron scattering (SANS) to measure the instantaneous spin-pair correlation function. Thus SANS provides a unique window to understanding the basic magnetic structure and dynamics in these nanoscale materials.

The sample examined in this study was prepared using RF magnetron sputtering, by co-deposition of Fe and  $\text{Al}_2\text{O}_3$  from a single mixed target onto thin  $\text{Al}_2\text{O}_3$  substrates kept at  $200^\circ\text{C}$ , resulting in a film approximately  $7\mu$  thick. The granular microstructure was confirmed by transmission electron microscopy, which reveals a narrow distribution of Fe particle sizes around 3 nm in diameter. The film composition of 35 vol% of Fe is well below the granular percolation concentration ( $\approx 60$  vol%), and, therefore, contains well-isolated particles [2]. X-ray diffraction analysis shows that the particles retain the body-centered cubic structure of bulk  $\alpha\text{-Fe}$ . Magnetic hysteresis loops obtained at  $T = 5$  K show a clear ferromagnetic behavior, with 60% remanent magnetization and a coercivity of about 600 Oe. For our sample,

the blocking temperatures  $T_B$  above which the particles become superparamagnetic are 75 K for SQUID measurements (peak in the zero-field-cooled susceptibility and onset of irreversibilities) and 210 K for MS measurements (onset of magnetic hyperfine splitting). Above  $T_B$ , little information on the magnetic ordering can be obtained by these methods.

The SANS samples consisted of many film layers superposed in an aluminum sample holder, resulting in a total sample thickness of more than  $100\mu$ . The temperature of the sample was varied between 15 K and 350 K, and the scattering intensity was obtained over the range of wavevector transfers ( $Q$ ) from  $0.17$  to  $1.5\text{ nm}^{-1}$  using an incident neutron wavelength of  $0.5\text{ nm}$ . A background spectrum was obtained at 425 K and subtracted from the low-temperature data, so that only the temperature-dependent magnetic scattering was analyzed. In the high- $Q$  region, the data is well described by a single Lorentzian-squared scattering function. Preliminary results on data obtained at longer neutron wavelengths suggest that this scattering is essentially wavelength-independent, i.e., that no inelasticity corrections are required in the analysis. We also expect the inter-particle fluctuations to be sufficiently slow (based on Mossbauer and bulk magnetization) that the SANS can measure the instantaneous correlation function between particles. If the Lorentzian-squared cross-section is a true representation of the instantaneous inter-particle correlation function, it is different than the Lorentzian form seen in bulk magnetic systems [3]. This may be related to the finite extent of the strongly-correlated magnetic regions in our granular sample.

At the smallest wavevector transfers, we find additional intensity, which we model by

adding a simple  $1/Q^2$  term to the scattering. Thus excellent fits to the data are obtained using:

$$I(Q) = \frac{A}{(Q^2 + \kappa^2)^2} + \frac{B}{Q^2} \quad (5)$$

where  $\kappa = 1/\xi$  is the inverse correlation length. The  $1/Q^2$  term corresponds to a Lorentzian cross-section with a near-zero inverse correlation length, thus reflecting correlations on a scale larger than what can be measured in our experiment (roughly a few tens of nm's). It is important to note, however, that the form of this cross-section is not unique, and that further refining of the data analysis is necessary to pinpoint the functional form and correlation length function associated with the low-Q scattering.

The Lorentzian-squared amplitude  $A$  is shown in figure 1 as a function of temperature. This amplitude is seen to decrease with decreasing temperature, suggesting that this component of the scattering is dynamic in origin. The decrease is sharp below 200 K, flattening out near zero below about 120 K. In figure 1 we also plot the correlation length  $\xi = 1/\kappa$  which shows a related temperature dependence. Starting at room temperature in the 1 nm range,  $\xi$  increases only slightly with decreasing temperature until about 200 K, below which a rapid increase is observed. However, instead of a divergence of  $\xi$ , we observe a saturation at about 4 nm, very close to the average particle size. By contrast, the amplitude  $B$  of the Lorentzian component to the scattering is constant and nearly zero at high temperatures. As  $T$  is decreased below 200 K,  $B$  begins to increase and rises sharply below 75 K, a behavior typical of order parameter scattering. Because of the long correlations lengths associated with this scattering, it is suggestive of inter-particle ordering.

The SANS results (fig. 1) suggest that the magnetic scattering at high temperatures ( $T > 200$  K) is due to spin fluctuations within the particles. Below 200 K, these fluctuations are slowly frozen out, with increasing correlation of the spins until the correlation length saturates near the particle size. As the intraparticle order

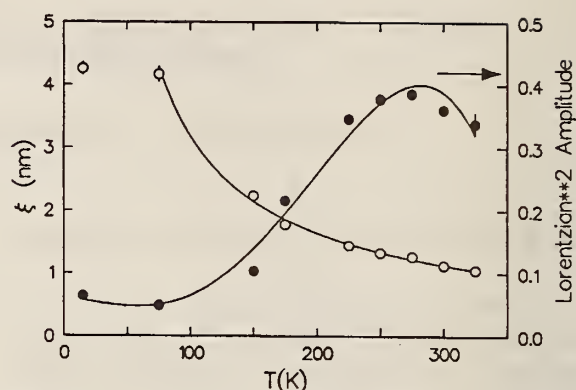


Figure 1. Amplitude  $A$  (filled circles) and correlation length  $\xi$  (open circles) associated with the Lorentzian squared term in the small-angle neutron magnetic scattering from 3 nm Fe particles (see eq. 1 in text), as a function of temperature. At low temperatures, the decrease of  $A$  suggests that this component is dynamic in origin, and a saturation of  $\xi$  is observed near the particle size. The lines are drawn to guide the eye.

increases, correlations develop between particles and increase as the temperature is lowered. Further SANS experiments, including a study of the dependence of the scattering on an externally applied magnetic field, are already under way to better characterize the low-Q component of the scattering, extract an Fe particle size distribution and to further understand the role of spin fluctuations in the scattering.

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# SCALING BEHAVIOR OF THE GENERALIZED SUSCEPTIBILITY IN $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$

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Motivated by the observation in both the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{6+y}$  series that the spin fluctuations at low energies have comparable strengths in antiferromagnetic, spin glass and superconducting samples, we have made a detailed study of the instantaneous and dynamic spin fluctuations for a crystal of  $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_4$  which is in the intermediate spin glass regime. We find that the instantaneous correlations are well described by theory for the 2-d Heisenberg model in the quantum disordered regime [5,6]. The spin-spin correlation length is  $\sim 40 \text{ \AA}$  and is temperature dependent below 300 K. Studies of the dynamics in the  $\text{CuO}_2$  plane reveal that the fluctuations are centered about the  $(\pi, \pi)$  position (square lattice, unit lattice constant notation) with negligible weight at other high symmetry positions such as  $(\pi, 0)$  and  $(2\pi, 0)$ . Our essential new result is that we find that the integrated response around  $(\pi, \pi)$  as a function of temperature  $T$  exhibits a simple scaling behavior in  $\omega/T$  for temperatures  $10 \text{ K} \leq T \leq 500 \text{ K}$  and energies  $4.5 \text{ meV} \leq \omega \leq 12 \text{ meV}$ .

The static measurements were carried out on a two axis spectrometer (BT-4) at NIST with incident neutron energy  $E_i = 30.5 \text{ meV}$  and collimator configuration 40'-20'-S-20'. The sample was oriented in the  $(h, k, 0)$  plane and scans were carried out across  $(h, 0.38, 0)$ . As discussed previously (ref. 1) in this geometry one automatically integrates over the 2-d spin fluctuations which have energies  $-T < \omega < 30.5 \text{ meV}$ . The inelastic measurements were carried out on a triple axis spectrometer (BT-9) with fixed incoming neutron energy  $E_i = 30.5 \text{ meV}$  and collimator configuration 40'-40'-S-40'-80'. The sample was oriented with  $[0, 1, 0]$  vertical so that the entire 2-d in-plane reciprocal lattice

could be studied. Pyrolytic graphite (002) was used as both monochromator and analyzer.

For a Heisenberg system, the neutron magnetic cross section is proportional to

$$S(\vec{q}, \omega) \propto \frac{1}{1 - e^{-\omega/T}} \text{Im}\chi(\vec{Q}, \omega). \quad (1)$$

A full-integration of equation 1 over energy yields the instantaneous spin-spin correlation function

$$S(\vec{Q}) = \frac{1}{2\pi} \sum_{\vec{r}} e^{i\vec{Q} \cdot \vec{r}} \langle \vec{S}_{\vec{0}} \cdot \vec{S}_{\vec{r}} \rangle. \quad (2)$$

Our experimental technique and method of analysis for the energy integrating measurements are identical to those discussed in ref. 1. We find that the static structure factor is peaked at  $(1, 0, 0)$  indicating that the local magnetic order is commensurate with the lattice. Fits of the measured structure factor to a 2-d Lorentzian show that the inverse correlation length  $\kappa$  is nearly independent of temperature from 10 K to 300 K and then increases gradually with increasing temperature above room temperature. The spin correlation length below room temperature is about  $40 \text{ \AA}$  and there are no evident effects on the spin correlations from the weak localization effects which typically set in below approximately 80 K.

We performed a series of inelastic scans at 6 meV at temperatures between 10 K and 300 K. We observed that the peaks are sharp and symmetric and that the background is relatively flat and featureless. Thus we are able to extract integrated intensities quite reliably. We carried out scans in both the longitudinal and transverse

directions through (100) for temperatures between 10 K and 500 K at energies of 4.5, 6.0, 9.0 and 12.0 meV. We also surveyed reciprocal space extensively at 10 K and 300 K. We found no significant scattering above background at any other place in reciprocal space including especially the  $(1/2, 0, 1/2)$  and  $(1,0,1)$  positions.

The resolution corrected 2-d integrated intensities as a function of temperature, In each case, peak at a temperature of  $T \approx 2\omega$ . This suggests that one should replot the data in a scaled form in terms of  $\omega/T$ . Since most theories and many derivative quantities involve  $\text{Im}\chi^\alpha(\vec{Q}, \omega)$  we have used eq. (1) to convert the measured  $\int_{(\pi,\pi)} d\vec{Q} S^\alpha(\vec{Q}, \omega)$  to  $\int_{(\pi,\pi)} d\vec{Q} \text{Im}\chi(\vec{Q}, \omega)$ . We have normalized the data and have chosen the overall scale such that the integrated susceptibility for  $\omega/T > 1$  is  $\sim 1$ . The results are plotted in figure 1.

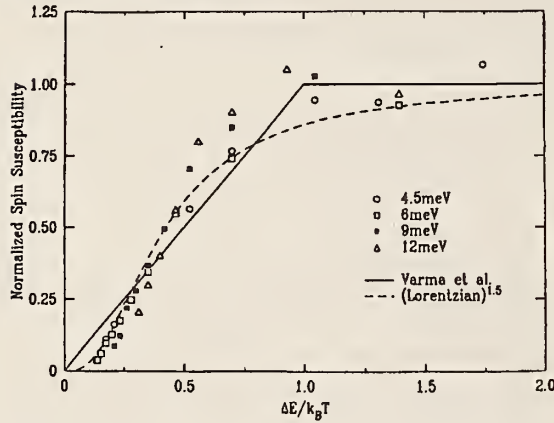


Figure 1. Normalized integrated spin susceptibility around  $(\pi, \pi)$  as a function of the scaling variable  $\Delta E/k_B T$ . The lines are the predictions of marginal Fermi liquid theory (solid line) and a fit to a heuristic power of Lorentzian form as discussed in the text (broken line).

We see that all of the data for temperatures between 10 K and 500 K and energies between 4.5 meV and 12 meV fall on a single universal curve when plotted in this fashion. This scaling occurs in spite of the fact that the correlation length is nearly independent of temperature over the entire temperature interval. We also note that there is no difference for data at temperatures above and below 80 K. Thus  $\text{Im}\chi(\vec{Q}, \omega)$ , along with the static correlations, is insensitive to effects of weak localization, as one might have expected on physical grounds since

weak localization largely involves the behavior of the carrier wave functions at large distances.

There also exists a more limited set of data for  $\text{YBa}_2\text{Cu}_3\text{O}_{6+y}$  at energies of 3, 6, and 8.3 meV for  $y = 0.45, 0.4$  and  $0.5$  respectively (ref 2). All three samples exhibit disordered magnetic states and are, at least in part, superconducting at low  $T$ . These data, which cover the range  $0.1 \leq \omega/T \leq 5$  fall on the same universal curve within the errors as that shown in figure 1. Thus our results appear to be quite general.

The only model we are aware of which predicts behavior anything like that shown in figure 1 is the "marginal" Fermi liquid hypothesis of Varma et al. [3]. Their model assumes,

$$\text{Im}\chi(\vec{Q}, \omega) \sim \begin{cases} \omega/T & \text{for } |\omega| < T \\ 1 & \text{for } |\omega| > T \end{cases} \quad (3)$$

and that  $\chi$  is weakly  $\vec{Q}$  dependent. Clearly, since  $\text{Im}\chi$  is sharply peaked about the  $(\pi, \pi)$  position the latter assumption is incorrect for low carrier concentrations. The hypothesized general behavior in  $\omega/T$  is, nevertheless, reasonably close to our experimental results. It is, however, clear from figure 1 that for  $\omega/T < 1$  the Varma et al. *ad hoc* assumption that  $\text{Im}\chi \sim \omega/T$  is not quantitatively correct. Instead our data require  $\text{Im}\chi \sim (a/T)^\alpha$  with  $\alpha \approx 3$  although  $\text{Im}\chi \sim (\omega/T)^2$  this exponent is poorly determined so that  $\alpha$  could range between 2 and 5. Thus, the effect of the 4% holes on  $\text{Im}\chi(\vec{Q}, \omega)$  is threefold. First, the spin-spin correlation length is reduced to 4 Å for  $T < 300$  K. Second, the  $1/\omega$  spin wave divergence as  $\omega \rightarrow 0$  is suppressed. Third, the spin fluctuations with energies  $\omega < T$  are severely diminished in amplitude like  $(\omega/T)^\alpha$  with  $\alpha \approx 3$ .

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# MAGNETIC CORRELATIONS AND ENERGY GAP IN SUPERCONDUCTING YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub> WITH T<sub>c</sub> = 53 K

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Over the past two years, inelastic-neutron-scattering studies have demonstrated the existence of dynamic magnetic correlations in superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> single crystals [1-4]. The data show that the imaginary part of the spin susceptibility,  $\chi''(Q, \omega)$ , is characterized in reciprocal space by a broad peak centered about the 2-d antiferromagnetic (AF) zone center, which in three dimensions forms the tetragonal rod  $Q_{AF}(\frac{1}{2}, \frac{1}{2}, \ell)$  measured in reciprocal lattice units (r.l.u.). For  $x \geq 0.5$  this peak width corresponds to a spin-spin correlation length on the order of twice the lattice spacing. As for the frequency dependence, the usual  $1/\omega$  behavior observed for spin waves in the antiferromagnetic phase is strongly suppressed at low frequencies. It has been shown that the observed magnetic cross section is consistent with a model in which antiferromagnetic spin fluctuations are heavily overdamped due to the short correlation length.

In addition to the overdamping of the low-frequency excitations, Rossat-Mignod et al. [5] have reported a temperature-dependent energy gap in superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> crystals with  $x = 0.51$  and  $0.69$  ( $T_c = 47$  and  $59$  K, respectively). They observed the gap in measurements of the frequency dependence of  $\chi''$  at  $Q_{AF}$ . Recently, Bulut and Scalapino [6] have pointed out that they obtain a pseudogap in  $\chi''$  precisely at  $Q_{AF}$  from a random-phase approximation (RPA) analysis of the normal-state properties of a 2-d Hubbard model; the gap occurs for kinematic reasons and does not appear at the incommensurate positions where their theoretical  $\chi''$  peaks. We have performed measurements on a single crystal with  $x = 0.6$  and  $T_c = 53$  K which convincingly demonstrate that the energy gap exists not only at  $Q_{AF}$ , but all along the zone diagonal [7]. At 10 K the  $Q$ -dependent magnetic peak vanishes (within experimental error) for energies  $\Delta E \leq 5$  meV.

Figure 1 shows several representative constant-E scans as a function of the in-plane momentum transfer taken along the zone diagonal ( $h, h, 1.8$ ) at energy transfers of 5, 9, and 12 meV at 10 K. Each scan was fit to a Gaussian line shape plus a constant sloping background, the sum of which is indicated by a solid line. Clearly the most striking feature is the absence of a measurable  $Q$ -dependent magnetic cross section at 5 meV. An identical scan at 3 meV also revealed no sign of a peak. In spite of the low counting rates associated with the magnetic signal, a clear and well-defined cross section is seen to emerge at 9 meV, becoming even more prominent at 12 meV. The difficulty inherent in these measurements becomes apparent when one realizes that the magnetic signal at 9 meV, counting 15 mins per point, is only  $\sim 30$  counts above a background of  $\sim 60$  counts. The low counting rate stems in

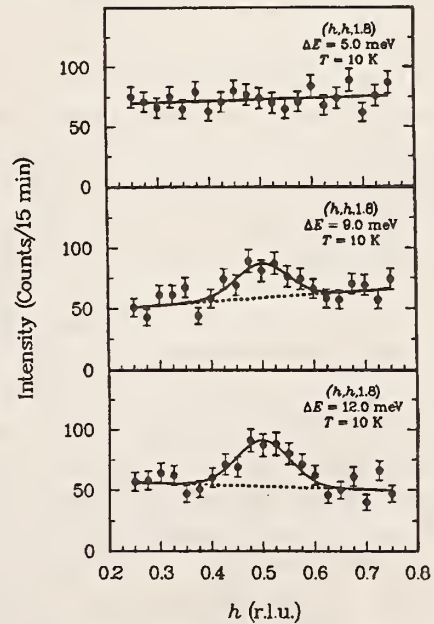


Figure 1. Constant-E scans measured along ( $h, h, 1.8$ ) at 5, 9, and 12 meV at 10 K, using a fixed incident neutron energy of 30.5 meV. Solid lines represent best fits to a Gaussian line shape.  $h$  is measured in reciprocal lattice units (r.l.u.), where  $1 \text{ r.l.u.} = 23\text{nm}^{-1}$ .

part from the very short spin-spin correlation lengths  $\xi$  present in superconducting samples. For  $x = 0.6$ , the constant-E scans at 10 K have full widths at half maximum (FWHM) of order  $\sim 0.12 \pm 0.02$  r.l.u. which implies a correlation length of only  $\xi \sim 0.7 - 0.9$  nm.

The complete set of measurements at 10 K is summarized in figure 2 where the 1-d q-integrated intensity of constant-E  $(h,h,1.8)$  scans is plotted as a function of energy transfer. The magnetic intensity is zero within experimental error up to 5 meV at 10 K. Above this energy, the spectral weight of the spin fluctuations begins to increase until it appears to saturate between 12 and 15 meV. The size of the gap is therefore taken to be  $\sim 5$  meV ( $\sim 60$  K), which is of order  $T_c$ . These data are consistent with those presented by Rossat-Mignod [5] for two samples corresponding to  $x = 0.51$  and  $0.69$ . The gap energy of 5 meV for  $x = 0.6$  is nicely bracketed by these two samples having both higher and lower oxygen contents. The size of the gap observed at low temperature in these samples appears to change rapidly with oxygen content, but shows little correlation with  $T_c$ .

Rossat-Mignod et al. [5] point out the similarity of the temperature dependence of  $\chi''(Q_{AF}, \omega)$  for small  $\omega$  and the unusual decrease of  $1/T_1$  below 100 K for  $^{63}\text{Cu}$  measured the NMR nuclear relaxation rate in 60-K material [8], but associating the spin-fluctuation gap with the normal-state behavior of  $1/T_1$  raises more questions than it answers. If the low-temperature gap develops above  $T_c$ , is it related to the superconductivity or is it a normal-state property? Bulut et al. [8] found a gaplike depression for integrated inelastic-scattering intensities at low temperature in their RPA analysis of a 2-d Hubbard model. In a more recent study, Bulut and Scalapino [6] found a pseudogap in  $\chi''(Q, \omega)$  at  $Q = Q_{AF}$ . By contrast, the data in figure 2 appear to indicate a true gap at 10 K in the  $x = 0.6$  sample along the entire zone diagonal, not just at the point  $Q = (\frac{1}{2}, \frac{1}{2}, 1.8)$ . If the gap observed by neutron scattering is connected to superconductivity, why is it so small and why does it change so rapidly with small changes in  $T_c$ ? Much more experimental work will be needed before these questions can be resolved.

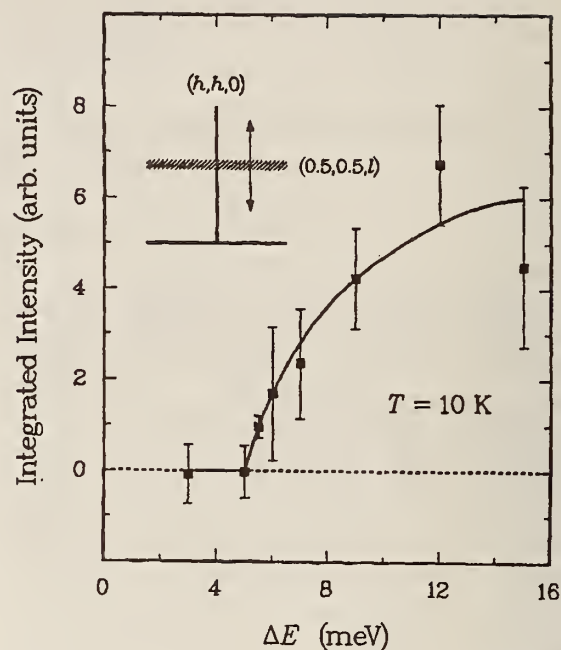


Figure 2. Frequency dependence of the magnetic cross section. Data points are the integrated intensities from Gaussian fits to  $(h,h,1.8)$  constant-E scans as shown schematically in the inset. Each scan was corrected for a constant sloping background and corrected for the spectrometer resolution. The solid line is a guide to the eye.

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MAGNETIC ORDER OF Cu IN  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ 

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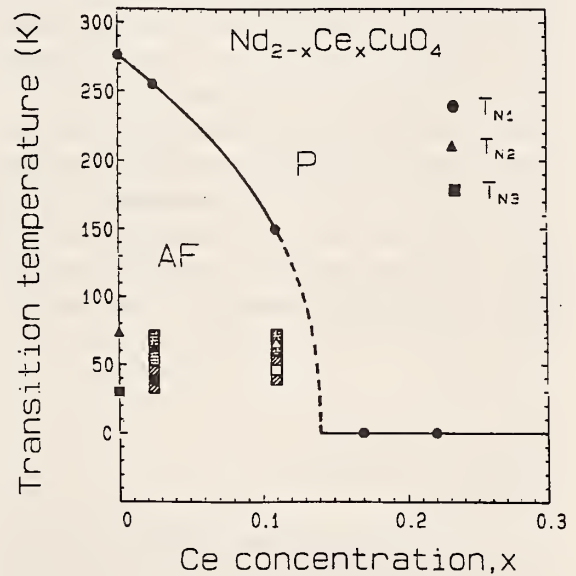
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The magnetic properties of the electron superconducting systems  $\text{R}_{2-x}\text{Ce}_x\text{CuO}_4$  ( $\text{R} = \text{Nd}$ ,  $\text{Pr}$  or  $\text{Sm}$ ) have been recently studied by neutron diffraction techniques[1-4]. The Cu spins in the parent materials  $\text{R}_2\text{CuO}_4$  order antiferromagnetically at relatively high temperatures ( $\sim 280$  K). For the  $\text{Nd}_2\text{CuO}_4$  system two spin reorientation transitions have been observed at 75 and 30 K, and there is a substantial interaction between the Cu and Nd sublattices [2]. However, these spin reorientation transitions are not observed in  $\text{Pr}_2\text{CuO}_4$  and  $\text{Sm}_2\text{CuO}_4$  [4]. Here, we report measurements of the Cu magnetic ordering in  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ . It is found that increasing the Ce concentration reduces the Néel temperature and site-averaged ordered Cu moment, and superconductivity is suppressed for  $x \geq 0.14$ . This behavior is qualitatively similar to the behavior observed in other oxide superconductors, but the rate of suppression is substantially less than in the related hole-type systems such as  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ .

Unpolarized neutron diffraction data were taken on single crystals of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  with  $x = 0.0, 0.025, 0.11, 0.17$  and  $0.22$ . Long-range antiferromagnetic order for Cu is observed in crystals with  $x = 0.0, 0.025$  and  $0.11$ . All the observed magnetic Bragg peaks in these crystals can be indexed as  $(h/2\ k/2\ l)$  based on the tetragonal chemical unit cell. The nearest neighbor spins in the Cu-O layers are antiparallel; however, the spin direction between layers can be either collinear or noncollinear [5]. The Néel temperatures ( $T_{N1}$ ) were obtained from the temperature dependence of the  $(\frac{1}{2}\ \frac{1}{2}\ 1)$  Bragg peak. The Néel temperature decreases with increasing Ce concentration  $x$ , which is shown in the phase diagram in figure 1. This phase diagram is slightly different from the one for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  [6] (hole doped), where an increase in Sr doping destroys the antiferromagnetic ordering more rapidly. The site-averaged ordered moment of the Cu spins

also decreases with increasing  $x$ . The temperature dependence of the  $(\frac{1}{2}\ \frac{1}{2}\ 1)$  magnetic Bragg peak was measured for both cooling and warming in the pure sample, and there was no indication of thermal hysteresis effects, in contrast to a previous report [3].



**Figure 1.** Magnetic phase diagram for  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  as a function of Ce concentration  $x$ . Shown are the regions of antiferromagnetic order (AF) and paramagnetic (P) behavior. The spin reorientation transition temperatures are taken as the mid point in the transition region, while the bars indicate the width of the transitions.

In the pure sample two spin reorientation transitions are observed at  $T_{N2} = 75$  K and at  $T_{N3} = 30$  K. At  $T = T_{N2}$  all the Cu spins rotate by  $\pi/2$  about the  $c$  axis, and they rotate back to their original direction at  $T = T_{N3}$ . Both spin reorientation transition temperatures increase with magnetic field at the rate of about 1.2 and 0.8 K/T, respectively [7]. These transitions can be most easily observed by looking at the temperature dependence of the  $(\frac{1}{2}\ \frac{1}{2}\ 0)$  peak intensity because this Bragg peak has non-zero intensity only between  $T_{N2}$  and  $T_{N3}$ .

The temperature dependence of the  $(\frac{1}{2}\frac{1}{2}0)$  magnetic Bragg peak is shown in figure 2 for  $x = 0, 0.025$ , and  $0.11$ . In addition to the decrease in  $T_N$  and the ordered moment via Ce doping, we see that the  $(\frac{1}{2}\frac{1}{2}0)$  intensity is strongly reduced by adding Ce. In fact in order to compare these data on the same graph, we have scaled the intensities by dividing by the square of the maximum site-averaged ordered Cu moment observed at each Ce concentration. Even with this normalization we see that the intensity drops off rapidly with increasing Ce concentration. We interpret this as a reduction in the fraction of the Cu spins which participate in the spin reorientation. The data also show that the transitions for the doped samples are not nearly as sharp as for the pure sample ( $x = 0.0$ ), which is likely caused by the site randomness of the Ce in the sample. The spin reorientation transition temperatures  $T_{N2}$  and  $T_{N3}$  are also shown in figure 1, where  $T_{N2}$  and  $T_{N3}$  are taken as the center point in the transition region, and the bars indicate the start and end points in the transition region.

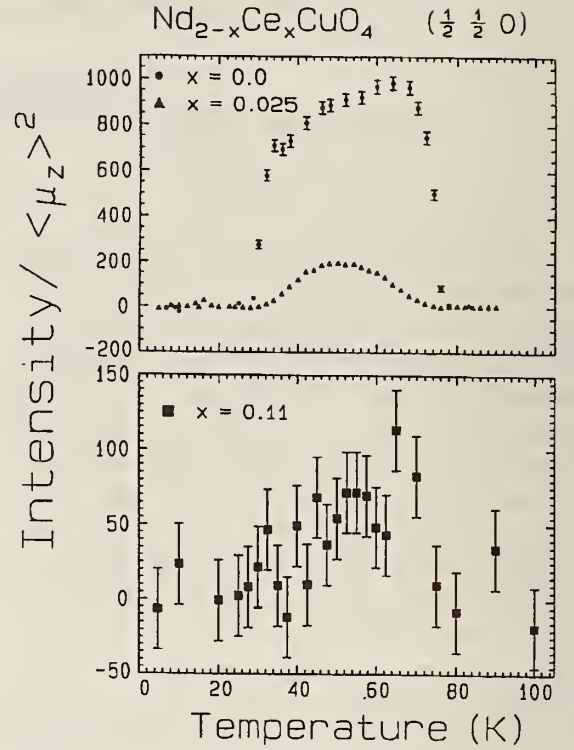


Figure 2. Temperature dependence of  $(\frac{1}{2}\frac{1}{2}0)$  magnetic Bragg peak for  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  for various Ce concentration  $x$ . These plots show the spin reorientation transitions.

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## TWO-DIMENSIONAL MAGNETIC CORRELATIONS AND MAGNETIC ORDERING OF Dy IN DyBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>

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The magnetic ordering of the rare earth ions in the layered superconducting oxides has been of particular interest because of the 2-d magnetic behavior these materials display [1-3]. In the RBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (*R* = rare earth) materials of direct interest here, the 2-d behavior originates naturally from the crystallography; there is only one rare earth ion per chemical unit cell, and the *c*-axis is three times as long as the *a* and *b* axes. Powder neutron diffraction experiments on ErBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> [2] were the first to confirm 2-d behavior of the rare earth ions in the RBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> system. Though the Er magnetic system is 2-d in character, when strong 2-d correlations develop in the *a-b* plane a weak interaction along the *c*-axis induces 3-d long range order at  $T_N = 0.618$  K [1]. The Dy [4], Nd [5] and Gd [6] systems have also been investigated with powder neutron diffraction, but these studies have mainly concentrated on the 3-d magnetic structures.

In this article we report measurements on a single crystal of DyBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. Above the 3-d ordering temperature we observe a rod of scattering along  $(\frac{1}{2} \frac{1}{2} q_z)$ , which directly demonstrates the 2-d character of the system. At low *T* the system is characterized by an antiferromagnetic structure with wave vector of the form  $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ , corresponding to antiferromagnetically coupled spins along all three crystallographic directions.

Above the ordering temperature the 2-d rod of scattering originates from critical fluctuations, while below  $T_N$  it originates from low energy magnetic excitations. In the quasielastic approximation the critical scattering is proportional to the wave-vector-dependent magnetic susceptibility  $\chi(q)$ . For a 2-d system in the Ornstein-Zernike approximation

$$I(q)_{\text{diffuse}} \propto c(q) \propto (\kappa^2 + q_x^2 + q_y^2)^{-1}$$

where  $\kappa$  is the inverse correlation length within the *a-b* plane. Thus, in a 2-d system we expect to see critical scattering about the reciprocal lattice positions as in the 3-d case, with the important difference that in the 2-d case the critical scattering should be independent of  $q_z$ , so one should see a rod of scattering extending along  $q_z$ .

Figure 1a shows a scan across the rod, just above the 3-d ordering temperature. This strong rod of scattering develops for temperatures  $\leq 2$  K. The linewidth of this peak is a measure of the inverse 2-d correlation length  $\kappa$ . Thus, by scanning across the rod at various temperatures we have observed the evolution of the magnetic correlations in the *a-b* plane. Also shown in this figure is a scan along the rod, which demonstrates that the scattering intensity is independent of  $q_z$ . Hence there are no significant correlations between spins in adjacent *a-b* planes, even though we are just above  $T_N$ .

Figure 2 shows the intensity at a point on the rod,  $(\frac{1}{2} \frac{1}{2} 1.2)$ , versus temperature. The rod starts to develop below about 2 K, and the intensity steadily increases with decreasing temperature until it peaks at  $T_N$ , when long range order sets in. Below  $T_N$  the intensity quickly decreases, presumably due to the sharp increase in the energy of the magnetic excitations, and the consequent decrease in their thermal population.

The temperature dependence of the sublattice magnetization obtained from the 3-d Bragg peak  $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$  is shown in figure 3, where the ordering temperature can be seen to be about 0.91 K. The 3-d ordering is simply being induced as a necessary consequence of the onset of long range order within the *a-b* planes [1]. This behavior is analogous to the 2-d and 3-d magnetic ordering of Er observed in ErBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> [1]. We have also observed

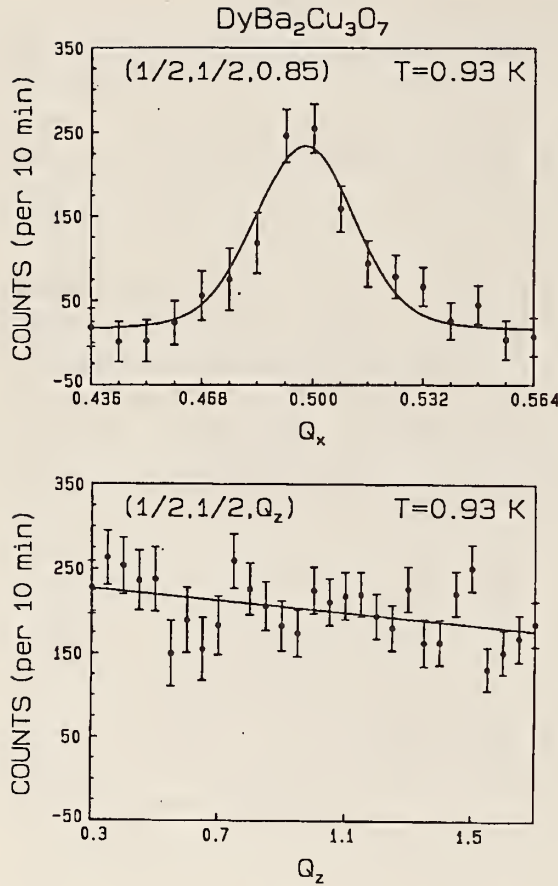


Figure 1. (a) A scan across the rod of scattering in reciprocal space, showing the 2-d character just above  $T_N = 0.91$  K and (b) a scan along the rod, showing that the scattering intensity does not vary significantly along  $Q_z$ . Hence there are no significant spin correlations between planes, even just above  $T_N$ . The slight decrease in intensity with increasing  $Q_z$  is due to the magnetic form factor.

magnetic Bragg peaks characterized by the wave vector  $(\frac{1}{2} \frac{1}{2} 0)$ , corresponding to ferromagnetically coupled spins along the  $c$ -axis and antiferromagnetic along the  $a$  and  $b$  directions, but this structure was only observed in oxygen deficient samples of Dy123. Therefore, we believe that the correct ground state spin configuration for fully oxygenated  $\text{DyBa}_2\text{Cu}_3\text{O}_7$  is  $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ .

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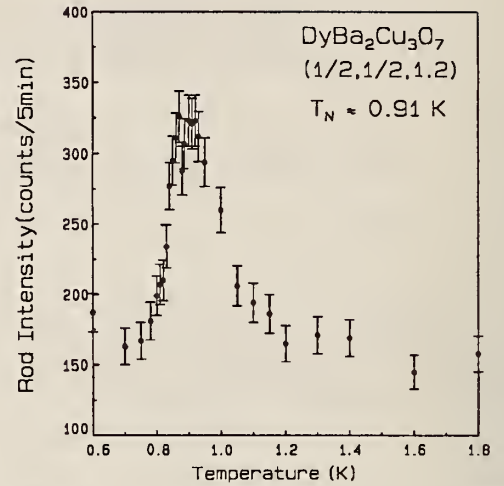


Figure 2. Rod intensity as a function of temperature.

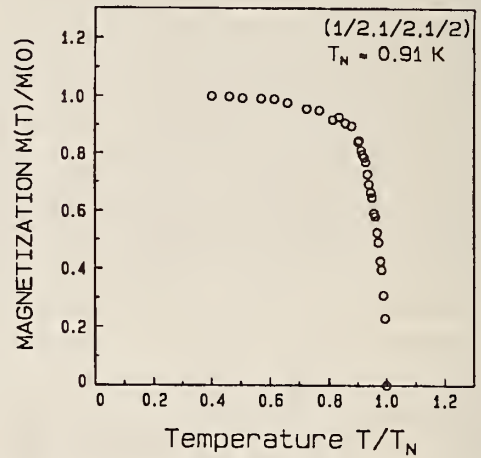


Figure 3. Sublattice magnetization vs temperature obtained from the  $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$  3-d magnetic Bragg peak, with  $T_N = 0.91$  K.

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## TWO-DIMENSIONAL BILAYER MAGNETIC ORDER OF Dy IONS IN $\text{Dy}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$

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A considerable amount of research has been done on the magnetic properties of the oxide superconductors [1] because on one hand the Cu spin fluctuations still stand as a candidate for the electron pairing mechanism, and on the other hand the rich phenomena of 2-d and 3-d magnetic order in these materials have stimulated considerable interest. We have been systematically investigating the nature of the rare-earth ordering in the  $\text{RBa}_2\text{Cu}_3\text{O}_7$  and  $\text{RBa}_2\text{Cu}_4\text{O}_8$  systems, and found that they are prototypical 2-d systems [2-4].

The present article reports our recent measurements on the  $\text{Dy}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  (2-4-7) material, which is directly related to the  $\text{DyBa}_2\text{Cu}_3\text{O}_7$  (1-2-3) and  $\text{Dy}_2\text{Ba}_4\text{Cu}_8\text{O}_{16}$  (2-4-8) systems. The Dy sublattice is shown in figure 1, where  $a = 3.864 \text{ \AA}$ ,  $b = 3.879 \text{ \AA}$ , and  $c = 50.26 \text{ \AA}$  [5]. The crystallographic anisotropy leads naturally to highly anisotropic magnetic

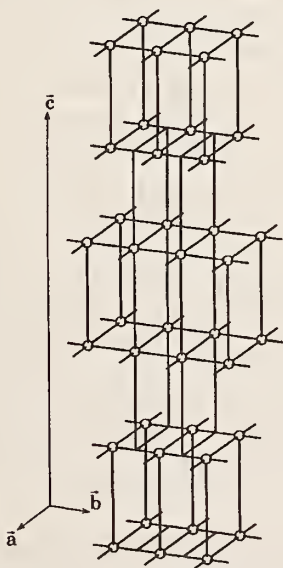
interactions and hence 2-d-like behavior. In addition, every other  $a$ - $b$  plane is shifted along the  $b$  direction by  $b/2$ . This, together with the crystal field anisotropy which forces the Dy spins along the  $c$ -axis, results in a cancellation of magnetic interactions between the shifted and unshifted layers.

The magnetic neutron powder diffraction data were taken with the standard subtraction technique, in which the scattering well above the ordering temperature is subtracted from the scattering at low  $T$ , to isolate the magnetic response of the system. A dilution refrigerator was employed to cool the powder samples down as low as 0.09 K. The samples were powder pellets with (onset) superconducting transition temperatures of  $\sim 60 \text{ K}$ . The 32 pellets have a total weight of 10 gm.

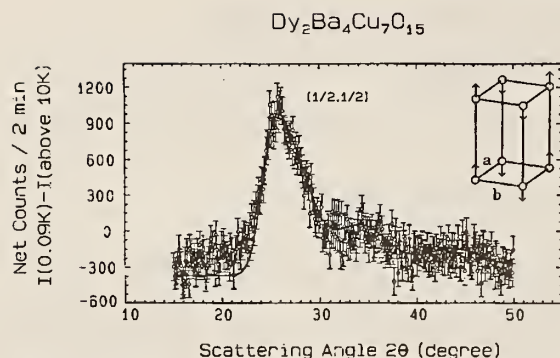
Figure 2 shows the magnetic scattering profile at  $T = 0.09 \text{ K}$ . The magnetic spin configuration is shown in the inset, where the spins are along the  $c$ -axis, and coupled antiferromagnetically in both  $a$  and  $b$  directions, but ferromagnetically in the  $c$  direction. The solid curve in figure 2 is the theoretical calculation based on such a 2-d coupled-bilayer magnetic structure shown in the inset. The Néel temperature is  $\sim 1.25 \text{ K}$ .

The spin structure in the  $a$ - $b$  planes observed in the  $\text{Dy}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  compound is the same as that found in the  $\text{DyBa}_2\text{Cu}_3\text{O}_7$  [6,7] and  $\text{DyBa}_2\text{Cu}_4\text{O}_8$  compounds [3]; nearest neighbors are antiparallel. When the Dy magnetic moments order at  $T_N$ , the behavior is 2-d in nature because the magnetic interaction in the  $c$  direction is much smaller than along  $a$  or  $b$ . This is due to the same crystallographic anisotropy (the Dy-Dy distance in  $c$  is  $\sim 3$  times that in  $a$ - $b$  plane).

Once the Dy spins are ordered two dimensionally, a coupling is induced between the two unshifted layers, which results in the



**Figure 1.** The Dy sublattice in the  $\text{Dy}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  compound. Every other layer is shifted along the  $b$ -axis by  $b/2$ , which is responsible for the cancellation of interplane magnetic interactions and ultimately the 2-d coupled-bilayer magnetic structure.



**Figure 2.** Magnetic scattering intensity for  $\text{Dy}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  at  $T = 0.09$  K. The solid curve is the calculated scattering intensity for a 2-d coupled bilayer system in which spins are pointing along the  $c$ -axis and antiferromagnetically coupled in both  $a$  and  $b$  directions, while along the  $c$  direction they are ferromagnetically coupled. The inset shows the magnetic structure, which is in principle repeated *ad infinitum* in the  $a$  and  $b$  directions, but is restricted to two layers along the  $c$  axis.

modulation of the usual "saw-tooth" shape of a 2-d powder diffraction profile. Between the shifted and unshifted layers, the magnetic (either dipolar or exchange) interactions are canceled by symmetry. Therefore no long range 3-d order occurs around the 2-d  $T_N$ . Indeed in our

experiment no 3-d order was observed to the lowest temperatures measured ( $\sim 90$  mK). An absence of 3-d order has also been found in the Dy 2-4-8 case [3], where a similar cancellation occurs between individual  $a$ - $b$  layers.

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## MAGNETIC ORDERING OF Sm IN $\text{Sm}_2\text{CuO}_4$

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The discovery of superconductivity in a new class of copper-oxide systems,  $\text{R}_{2-x}\text{Ce}_x\text{CuO}_4$  ( $R = \text{Nd}, \text{Pr}, \text{Sm}$ ) [1], has attracted considerable interest since these are the only copper-oxide systems known to date that carry electrons as the charge carriers, in contrast to the hole conduction observed in other high  $T_c$  copper-oxide systems. In addition to their transport properties, these materials together with their parent insulating compounds  $\text{R}_2\text{CuO}_4$  exhibit a variety of interesting magnetic behavior involving both the rare earth and the copper spins [2-6]. Two members of these electron-doped systems (Nd,Sm) [2,3] have displayed a coexistence of rare-earth magnetism

and superconductivity, thus providing an interesting situation to study the interplay between the two cooperative phenomena, particularly since there is no clear separation between the magnetic and the superconducting subsystems. It is, therefore, of central concern to elucidate the magnetic properties in these systems.

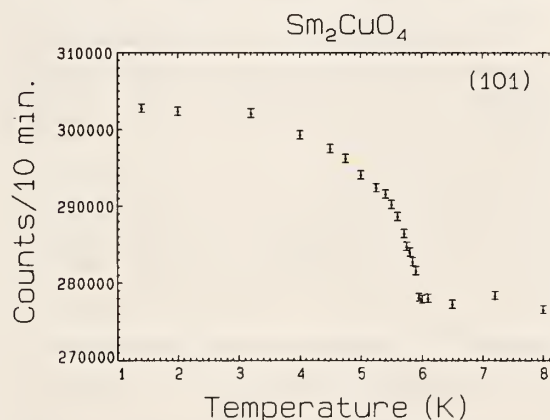
Neutron diffraction techniques have been carried out to investigate the magnetic properties of the  $\text{R}_2\text{CuO}_4$  compounds [3-6]. The Cu spins in these materials order at relatively high temperatures ( $\sim 280$  K) in a simple antiferromagnetic arrangement: the rare-earth ordering in the  $\text{Nd}_2\text{CuO}_4$  compound is particularly

interesting since it is found that the ordered Cu sublattice exhibits a substantial coupling to the Nd sublattice, thereby inducing the ordering of Nd ions [3]. As for the related  $\text{Pr}_2\text{CuO}_4$  compound, it has been suggested that a small Pr moment is induced, similar to that found in  $\text{Nd}_2\text{CuO}_4$  [5]. In this report we present the results of our investigations of the nature of the Sm ordering in the  $\text{Sm}_2\text{CuO}_4$  compound from neutron diffraction measurements.

A thin plate-like high-quality single crystal of  $\text{Sm}_2\text{CuO}_4$  weighing 66 mg was used, which is the same crystal used in our earlier studies of the Cu ordering [6]. Its growth and preparation techniques can be found in the literature [6]. The crystal needed to be very thin because the experiments must be done in transmission geometry, and Sm is highly absorbing. Unpolarized neutron diffraction data were taken with a wavelength of 2.358 Å on the BT-2 triple-axis spectrometer with a pyrolytic graphite PG(002) monochromator and a PG filter. The crystal was mounted in the  $(h,0,\ell)$  scattering plane and enclosed in a  $^3\text{He}$  cryostat.

Figure 1 shows the temperature dependence of the (101) Bragg peak intensity, and reveals a phase transition at  $T_N = 5.95$  K associated with long-range antiferromagnetic order of the Sm spins. This value of  $T_N$  is in good agreement with specific heat data [7]. The magnetic Bragg peaks below  $T_N$  share the same reciprocal lattice positions with the nuclear Bragg peaks, in fact, the scattering intensity of 275,000 counts/10 min shown in figure 1 is due to the (101) nuclear Bragg peak. Since the Miller indices of the magnetic Bragg peaks are integers, the magnetic unit cell is identical to the chemical unit cell. The Sm spin configuration consists of ferromagnetic sheets *within* the  $a$ - $b$  planes, with the spins in alternate layers aligned antiparallel. This spin configuration differs from the rare-earth spin structure observed in the related  $\text{Nd}_2\text{CuO}_4$  and  $\text{Pr}_2\text{CuO}_4$ , and in fact the ferromagnetic sheets of rare-earth ions in the  $a$ - $b$  plane are not found in any other copper-oxide systems. This prompts an interesting question as to how these ferromagnetic sheets affect the electrons in the Cu-O layers, which are involved in the superconductivity in the doped superconductor  $\text{Sm}_{2-x}\text{Ce}_x\text{CuO}_4$ .

We have also determined that the Sm spin direction is along the  $c$ -axis, which is perpendicular to the Cu spin directions; the Cu sublattice has already ordered at 280 K [6]. We observe no coupling between the Sm and the Cu spins, which is not surprising since the spin directions are orthogonal and the magnetic structures are different. This contrasts with the behavior observed in the related  $\text{Nd}_2\text{CuO}_4$  system, where the magnetic structures and spin directions are the same, and strong coupling is observed. We have also observed an increase in the Sm magnetic Bragg intensities below  $\sim 0.8$  K, which is currently under further investigation.



**Figure 1.** Temperature dependence of (1,0,1) Bragg peak intensity. The scattering intensity of 275,000 counts/10 min is due to the nuclear Bragg peak. The magnetic contribution can be seen as a rise in the intensity as the temperature goes below  $T_N = 5.95$  K.

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## OBSERVATION OF THE MAGNETIC FLUX LATTICE IN $\text{DyBa}_2\text{Cu}_3\text{O}_7$

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It is well known that in type-II superconductors when the applied magnetic field exceeds  $H_{C1}$  the magnetic flux becomes quantized inside the superconductor with flux quantum  $\phi_0 = h/2e$ , and the flux quanta form a 2-d triangular magnetic flux lattice (MFL). This MFL can be investigated by using  $\mu\text{SR}$  techniques, the Bitter decoration method, STM and small angle neutron scattering (SANS), for example. Each technique has its own merits, but neutron scattering data are the most representative of the bulk properties of the MFL. Although the MFL has been well studied for the low  $T_c$  superconductors [1], it is considerably more difficult to make measurements for the high  $T_c$  oxide superconductors because the London penetration depths in these materials are much longer and therefore the flux quanta overlap, making the lattice much more difficult to observe.

The observation of MFL in the oxide superconductors by neutron scattering was first reported by Forgan et al. in a single crystal of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  [2]. In this report we present the results of our preliminary measurements in a single crystal  $\text{DyBa}_2\text{Cu}_3\text{O}_7$  sample.  $\text{DyBa}_2\text{Cu}_3\text{O}_7$  was chosen because the Dy ion carries a magnetic moment and the crystal electrical field forces the moment direction to be along the  $c$ -axis. Thus when an external magnetic field is applied along the  $c$ -axis the Dy magnetic moments can be aligned, increasing the magnetic scattering. More importantly, it is the total magnetic flux that should be quantized, and this leads to a number of possible new phases [3]. It will also be interesting to investigate how

the MFL lattice interacts with the Dy ions. As a first step toward answering these questions, we carried out an exploratory experiment at the 8-m SANS. A wavelength of  $\lambda = 6 \text{ \AA}$  was used because Dy has a large absorption cross section and the neutron absorption rate is exponentially proportional to the wavelength. The coarse resolution configuration was used to achieve high incident beam intensity. The sample-detector distance was 360 cm. Under these conditions the minimum  $q$  observable is typically  $\sim 0.0083 \text{ \AA}^{-1}$ , and in order to bring the (10) MFL diffraction peak signal out of the shadow of the beam stop  $q_{10}$  needs to exceed this, where

$$q_{10} = 4\pi \left[ \frac{B}{2\sqrt{3} \phi_0} \right]^{1/2}.$$

We therefore chose  $H = 5 \text{ kOe}$ , which gives  $q_{10} = 0.0105 \text{ \AA}^{-1}$ . In addition, we moved the beam stop away from the usual beam stop center in order to reach smaller  $q$ 's on the side of the detector where the diffraction peak was expected.

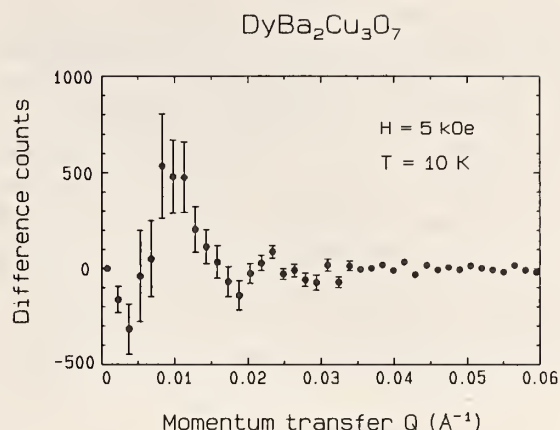
The sample was a fully oxygenated single crystal weighing 250 mg, and had the approximate dimensions of  $5 \times 5 \times 2 \text{ mm}^3$  with a superconducting (onset) transition temperature  $\sim 90 \text{ K}$ . This is the same crystal used in our diffraction measurements of the Dy magnetic ordering with  $T_N \approx 1 \text{ K}$  (see p. 27 in this report). Two sets of data were collected at each temperature, one with the sample field-cooled from above  $T_c$  and another with the sample zero-field-cooled. The zero-field-cooled data

were then subtracted from the field-cooled data to isolate the magnetic response. The observed signal was highly anisotropic, and an appropriate sector average was taken. The subtracted data taken at  $T = 10$  K are shown in figure 1, and reveal vortex scattering in the vicinity of  $q \sim 0.01 \text{ \AA}^{-1}$ , as expected. This scattering intensity also decreased with increasing temperature as expected for a vortex lattice.

The sample used in the present measurements was much thicker than desired for these vortex (SANS) experiments, so that substantial improvements in the intensity can be expected in the next phase of the experiment. It will also be important to compare these data with data for  $\text{YBa}_2\text{Cu}_3\text{O}_7$  where there is no rare earth moment. Further work is in progress.

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**Figure 1.** Field-cooled data subtracted from the zero-field-cooled data, for a temperature of  $T = 10$  K. The applied field is  $H = 5$  kOe, which yields a  $q_{10} = 0.0105 \text{ \AA}^{-1}$ . The data were collected for 3 1/2 hrs at each temperature.

## NEUTRON POWDER DIFFRACTION STUDY OF THE CRYSTAL STRUCTURES OF $\text{YSr}_2(\text{CoCu}_2)\text{O}_7$ , $(\text{Y}_{1-x}\text{Ca}_x)\text{Sr}_2(\text{CoCu}_2)\text{O}_7$ , AND $\text{YSr}_2(\text{GaCu}_2)\text{O}_7$

Q. Huang and A. Santoro  
and

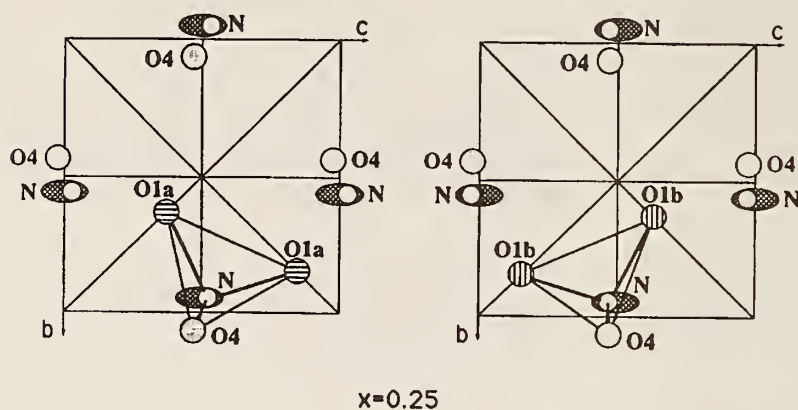
R. J. Cava (AT&T Bell Laboratories)

The structures of  $\text{YSr}_2(\text{Co Cu}_2)\text{O}_7$  and  $(\text{Y}_{1-x}\text{Ca}_x)\text{Sr}_2(\text{Co Cu}_2)\text{O}_7$  have been analyzed by neutron powder diffraction techniques. Both materials crystalize with the symmetry of space group  $\text{Ima}2$  and lattice parameters  $a = 22.7900(5)$ ,  $b = 5.4515(1)$ ,  $c = 5.4097(1) \text{ \AA}$  for  $\text{YSr}_2(\text{Co Cu}_2)\text{O}_7$  and  $a = 22.8266(7)$ ,  $b = 5.4312(2)$ ,  $c = 5.4048(2) \text{ \AA}$  for  $(\text{Y}_{1-x}\text{Ca}_x)\text{Sr}_2(\text{CoCu}_2)\text{O}_7$ . In the non-doped compound the Co ions substitute exclusively the copper ions located on the chain sites of the 1,2,3, parent structure,  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ . The coordination of Co is tetrahedral and the  $\text{CoO}_4$  tetrahedra form chains propagating in a zigzag fashion along the c-axis of the structure. The

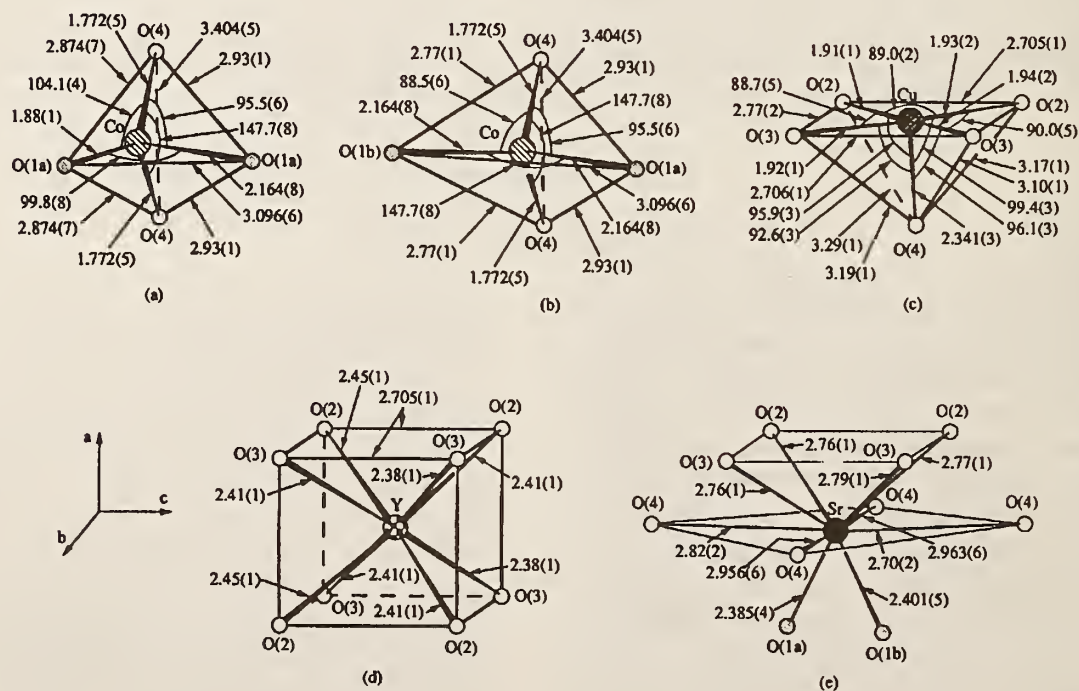
oxygen atoms of the CoO layers were found to be disordered over two sets of positions, O(1)a at  $1/4, y_o, z_o$  and O(1)b at  $1/4, y_o, 1-z_o$ , with occupancy factors of 0.62(4) and 0.38(4). In the case of the compound  $\text{YSr}_2(\text{Ga Cu}_2)\text{O}_7$  [1], our measurements show that this type of disordering is much less pronounced, with occupancy factors of 0.88(2) and 0.12(2). The presence of oxygen on the sites O(1)a and O(1)b creates a configuration of the chains of  $\text{CoO}_4$  tetrahedra such that two types of chains coexist, one being the mirror image of the other. The unusually high temperature factor of Co has been attributed to a splitting of the atom between two positions, symmetrical with respect to  $z = 0$ ,

along the c-axis. This configuration can be easily explained in terms of the disordering of the oxygen atoms over the positions O(1)a and O(1)b and the coordination requirements of cobalt (figs. 1 and 2). Our experimental results are consistent with the distribution of oxygen atoms on the layers CoO shown in figure 3. It can be shown that such configuration is closely related to that of the oxygen atoms located on the basal plane of the 1,2,3 superconductor for the  $O_7$  composition. The structure of the doped

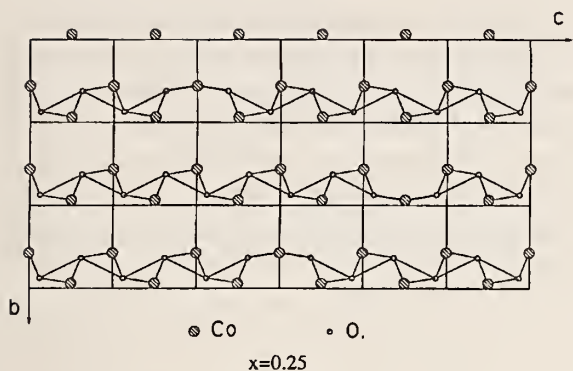
compound  $(Y_{1-x}Ca_x)Sr_2(CoCu_2)O_7$  is considerably more complicated than that of the nondoped material. Calcium substitutes yttrium, but cobalt seems to replace copper both on the chain sites and at the  $CuO_2$  planar sites. The oxygen atoms on the CoO layers seem to be disordered not only over the O(1)a and O(1)b sites, but also over the two sites generated from these by the operation of the mirror  $x, 1/2, z$ , perpendicular to the b-axis. Models for the local structure of this compound are still under investigation.



**Figure 1.** Atomic configuration of the layers CoO at  $x = 1/4$ . In this figure  $N = Co$ . The oxygen atoms O(1)a and O(1)b are co-planar with N, but the atoms O(4) belong to the SrO layers and are located above and below the plane of figure. The two diagrams show the two possible tetrahedra which form chains running parallel to the c-axis.



**Figure 2.** Coordination polyhedra of the metal ions in the structure of  $YSr_2(CoCu_2)O_7$ . Figure 2a represents the  $CoO_4$  tetrahedra forming the regular chains on the CoO layers and figure 2b the  $CoO_4$  tetrahedra interconnecting chains perpendicular to one another.



**Figure 3.** Model of the atomic structure of the CoO layer at  $x = 1/4$ . The atoms O(4) are not shown for clarity. The corner-sharing tetrahedra of oxygen atoms form two types of chains which are specular to one another. A possible way of interconnecting the chains is also shown in the figure.

### References

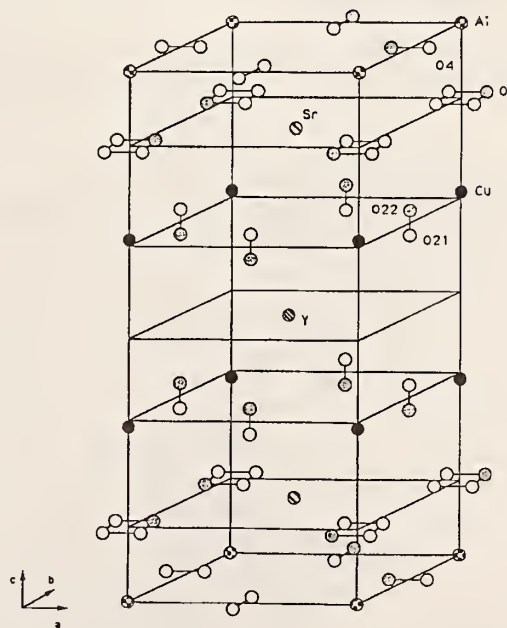
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## NEUTRON POWDER DIFFRACTION STUDY OF THE STRUCTURE OF $\text{YSr}_2(\text{AlCu}_2)\text{O}_7$

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and

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The structure of  $\text{YSr}_2(\text{AlCu}_2)\text{O}_7$  has been analyzed by neutron powder diffraction techniques. The compound crystallizes with the symmetry of space group  $P4/mmm$  and lattice parameters  $a = 3.8645(1)$  and  $c = 11.1139(3)\text{\AA}$ . A schematic representation of the unit cell is shown in figure 1. This structure is closely related to that of the 1,2,3 superconductor and to those of  $\text{YSr}_2(\text{GaCu}_2)\text{O}_7$  and  $\text{YSr}_2(\text{CoCu}_2)\text{O}_7$ . Like the Ga and Co ions in these last two compounds, also Al replaces exclusively the chain copper ions, assuming tetrahedral coordination and forming chains similar to those made by the  $\text{GaO}_4$  and  $\text{CoO}_4$  tetrahedra. Refinements of the structure show that practically all the oxygen atoms are disordered over the sets of positions indicated in figure 1. The models refined, and the order in which the refinements were made, are specified in table 1. The first case is the same as the structure of the parent 1,2,3 compound. In model 2, the oxygen atoms O(1) and O(4) are split along the  $a$ -axis,



**Figure 1.** Unit cell of the compound  $\text{YSr}_2(\text{AlCu}_2)\text{O}_7$ , showing the splitting of the oxygen atoms around their idealized positions corresponding to the structure of the 1,2,3 superconductor.

and in model 3 the extra atom O(42) is introduced with further improvement of the R-factors. In 4 the oxygen atoms O(1) are shifted along the mesh's diagonal, and finally, in model 5, based on space group P4/mmm, the atoms O(2) are split vertically, i.e. an extra atomic position is introduced in the structure for these atoms. The atomic disordering present in this structure results in many possible local configurations.

For example, the possible coordination polyhedra of the Al ions are illustrated in figure 2. Based on reasonable bond distances and angle, of these four possibilities only the tetrahedra II and III have to be taken into consideration (the other two have a too short O-O distance of 2.310 Å). The analysis of models for the coordination polyhedra of the other metal ions is still under way.

Table 1. Shifts of the oxygen atoms in  $\text{Sr}_2\text{YAlCu}_2\text{O}_7$ .

	1	2	3	4	5
O1	0, 0, z	x, 0, z	x, 0, z	x, x, z	x, x, z
O2	1/2, 0, z	1/2, 0, z	1/2, 0, z	1/2, 0, z	1/2, 0, z**
O3	0, 1/2, z	0, 1/2, z	0, 1/2, z	0, 1/2, z	
O41	0, 1/2, 0	x, 1/2, 0	x, 1/2, 0	x, 1/2, 0	x, 1/2, 0
O42			1/2, y, 0	1/2, y, 0	
a	3.8644(1)	3.8645(1)	3.8645(1)	3.8645(1)	3.8645(1)
c	11.1142(3)	11.1139(3)	11.1141(3)	11.1139(3)	11.1139(3)
V	165.97(1)	165.98(1)	165.98(1)	165.98(1)	165.98(1)
Rn	12.56	9.35	8.26	7.87	5.97
Rp	9.29	8.34	7.84	7.65	7.09
Rw	12.29	11.17	10.26	10.03	9.49
Re	4.49	4.49	4.49	4.49	4.49
$\chi$	2.74	2.49	2.29	2.23	2.11

\*Pmmm symmetry is used in 1,2,3, and 4, but set  $a = b$ ,  $z(\text{O2}) = z(\text{O3})$ , and  $x(\text{O41}) = y(\text{O42})$ .

P4/mmm symmetry is used in 5.

\*\*This atom is split along c.

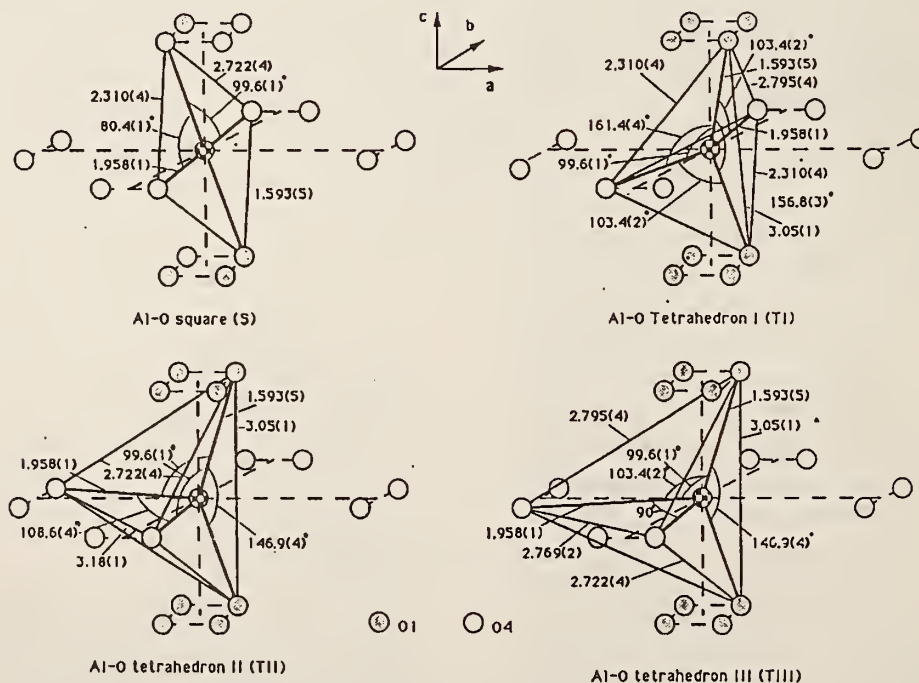


Figure 2. Possible coordination polyhedra around the Al ions. The first two cases have to be excluded because they result in unreasonably short O-O distances.

# Cu CHAIN AND PLANE ORDERING OF SINGLE CRYSTAL $\text{PrBa}_2\text{Cu}_3\text{O}_{6+x}$

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Alone of all the single-phase layered perovskites,  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  (Pr1237) is not superconducting [1]. Two possible explanations have been advanced to explain this behavior. One suggests that the Pr is mixed-valent with the electrons resulting from the oxidation of  $\text{Pr}^{3+}$  to  $\text{Pr}^{4+}$  filling holes in the conduction band [2]. The other explanation proposes that the  $f$  electrons of  $\text{Pr}^{3+}$  hybridize with the conduction electrons and thereby suppress the superconductivity [3]. In an effort to understand the effect of the Pr ion on the R1236+x system, we are studying the Cu and Pr magnetism in Pr1236+x. Previous neutron diffraction measurements on powder Pr1237 [4] showed that the Pr ordered at  $T_N \approx 17$  K, with a moment of  $0.74 \mu_B$  directed along the  $c$  axis.

We have measured a 11.5 mg single crystal of as-grown Pr1236+x on BT-2 and BT-6 over the temperature range  $4 \text{ K} < T < 340 \text{ K}$ . The crystal was aligned with  $hhl$  reflections in the scattering plane. Figure 1 shows room temperature transverse scans of the (006) and (113) structural Bragg peaks which indicate that the single crystal is of high quality.

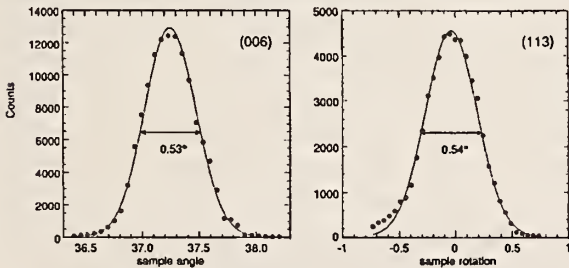


Figure 1. Transverse scans of the (006) and (113) reflections of Pr1236+x.

The Cu ordering in Y1236+x and Nd1236+x has been shown, by neutron diffraction [5], to take two forms (fig. 2). For *plane ordering*, in which only the Cu spins in the plane sites are ordered, only  $(\frac{m}{2} \frac{n}{2} l)$  reflections ("whole-integral" reflections) are observed. For *chain*

*ordering*, in which the Cu spins in both the plane and chain sites are ordered,  $(\frac{m}{2} \frac{n}{2} \frac{p}{2})$  reflections ("half-integral" reflections) are observed while the whole-integral reflections are greatly reduced in magnitude. For small  $x$ , the planes order for  $T \approx 500 \text{ K}$  and the chains order below  $100 \text{ K}$ .

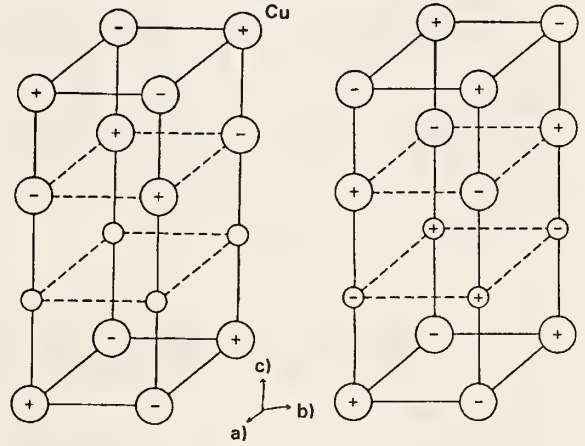


Figure 2. The basic spin structure for the Cu moments: (a) only plane Cu ordered and (b) both plane and chain Cu ordered.

For the present Pr1236+x crystal, we observed half-integral peaks at all the temperatures studied, which indicates that both the Cu chains and planes are ordered up to  $T = 340 \text{ K}$ . This is quite different from the behavior of the other R1236+x compounds, but a similar increase in the chain ordering temperature has been observed in the Co-substituted  $\text{YBa}_2(\text{Co,Cu})_3\text{O}_{6+x}$  system, where the Co ions preferentially occupy the chain sites [6]. Hence these data suggest that the presence of Pr not only affects the superconductivity but also strongly affects the Cu magnetism. The temperature dependence of the  $(\frac{1}{2} \frac{1}{2} \frac{3}{2})$  reflection is shown in figure 3, indicating a  $T_N$  near  $390 \text{ K}$ .

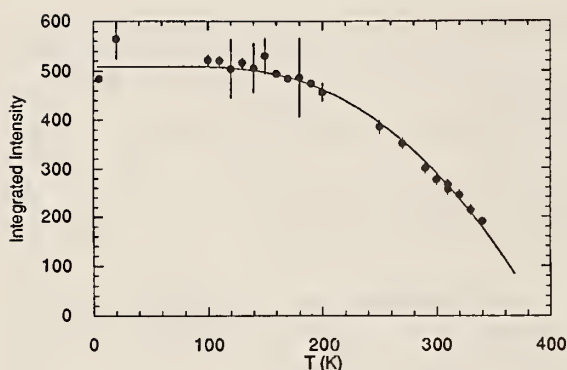


Figure 3. Temperature dependence of the  $(\frac{1}{2} \frac{1}{2} \frac{3}{2})$  integrated intensity, indicating  $T_N \approx 390$  K.

We observed a small significant decrease in the intensity of the  $(\frac{1}{2} \frac{1}{2} \frac{3}{2})$  reflection as  $T$  was decreased from 20 K to 5 K. This may be due to the onset of magnetic order for the Pr; however, further analysis is required to confirm this.

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## PHONON DENSITY-OF-STATES IN THE SUPERCONDUCTORS (Nd-Ce)<sub>2</sub>CuO<sub>4</sub> AND (Pr-Ce)<sub>2</sub>CuO<sub>4</sub>

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Since the discovery of high- $T_c$  superconductors the mechanism of the electron pairing in these systems has remained an open question. However, there are observations which suggest that phonons may play a major role in the formation of the superconducting state, particularly in the "moderate- $T_c$ " ( $\sim 30$  K) systems. For example, a substantial isotope effect has been reported in the  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  ( $M = \text{Sr}, \text{Ba}$ ) [1] system, and measurements of  $\alpha^2F(\omega)$  in  $(\text{Ba-K})\text{BiO}_3$  from point-contact-tunneling have been found to be in reasonable agreement with the measured phonon density-of-states from neutron scattering [2]. We have been investigating the phonon density-of-states in the 2-1-4 electron-superconductor systems using inelastic neutron scattering techniques. For the case of  $(\text{Nd-Ce})_2\text{CuO}_4$  we have found reasonable agree-

ment at low energies between the point-contact tunneling density-of-states data and our neutron measurements, suggesting that phonons are involved in the pairing mechanism in these systems [3]. We present here our measurements of the generalized phonon density-of-states (GPDOS) in the  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  and  $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$  superconducting materials, as well as the related insulating undoped systems.

Powder samples of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ ,  $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ ,  $\text{Nd}_2\text{CuO}_4$ , and  $\text{Pr}_2\text{CuO}_4$ , each weighing  $\sim 42$  g, were prepared by the usual methods found in the literature [4]. The neutron scattering experiments were carried out on the BT-4 triple-axis spectrometer and all measurements were done at 4.2 K. The measurements were taken in the energy loss mode with a fixed final energy using a Be-graphite-Be filter

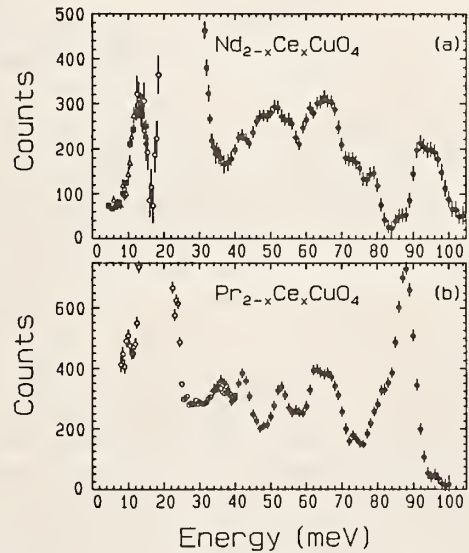
analyzer assembly and employing either a pyrolytic graphite PG(002) monochromator for low energy transfers ( $\leq 40$  meV) or a Cu(220) monochromator for higher energy transfers ( $\geq 36$  meV). In the case of  $(\text{Nd-Ce})_2\text{CuO}_4$ , the data were supplemented by the usual triple-axis technique for energies  $\leq 23$  meV, employing these two monochromators. The triple-axis technique has the advantage at low energy transfers of being able to collect data over a range of momentum transfers,  $\vec{Q}$ , and at larger values of  $|\vec{Q}|$ .

Figure 1a shows the observed scattering for energy transfers up to 105 meV in  $(\text{Nd-Ce})_2\text{CuO}_4$ . The region between 17 meV and 35 meV is dominated by two magnetic peaks whose intensities go beyond the scale of the figure thus prohibiting the determination of the phonon density-of-states in this region of energy. These magnetic peaks, as well as the 93 meV peak shown in the figure, originate from crystal-field excitations of the Nd ions. The phonon density-of-states spectrum extends only up to  $\sim 84$  meV. The observed phonon peak at 13 meV and another peak at  $\sim 40$  meV are in reasonable agreement with the peaks measured in the tunneling data [3]. The correspondence at higher energies between the tunneling and our data is at present not good, but we believe this reflects the extreme difficulty in obtaining quantitative tunneling data in the oxide-superconductors.

Figure 1b shows the density-of-states for  $(\text{Pr-Ce})_2\text{CuO}_4$ . The crystal-field transitions out of the ground state for the Pr ions occur at 88 meV and at  $\sim 18$  meV; the intensity of the low energy crystal field peaks for both systems goes beyond the scale of the figures. As illustrated there are substantial changes in the peak intensities in a region of energy between 30 and 60 meV as the material is changed from  $(\text{Nd-Ce})_2\text{CuO}_4$  to  $(\text{Pr-Ce})_2\text{CuO}_4$ . The broad feature around 53 meV narrows into a peak at 53 meV and the 40 meV peak intensity increases relative to the 53 meV peak. There is also a peak at  $\sim 36$  meV in the  $(\text{Pr-Ce})_2\text{CuO}_4$  compound which is not observed in the  $(\text{Nd-Ce})_2\text{CuO}_4$  data. Infrared reflectivity measurements on polycrystalline  $(\text{Pr-Ce})_2\text{CuO}_4$  show active IR modes at 33.6, 53.1, 62.6, and 68.4 meV corresponding to the motions parallel

to the c-axis [5]. However, direct identification with the GPDOS is difficult since IR techniques generally measure zone-center phonon modes, while substantial dispersion in all the phonon branches is expected, analogous to the related  $\text{La}_2\text{NiO}_4$  [6] where the dispersion relations have been measured in detail.

We also have observed substantial decreases in some of the phonon peak intensities as the material is changed from the parent insulating  $\text{Pr}_2\text{CuO}_4$  to superconducting  $(\text{Pr-Ce})_2\text{CuO}_4$ . It will be interesting to see the correspondence between our data for  $(\text{Pr-Ce})_2\text{CuO}_4$  and the tunneling data when they become available.



**Figure 1(a).** Generalized phonon density-of-states (GPDOS) in  $(\text{Nd-Ce})_2\text{CuO}_4$ , whose spectrum extends up to  $\sim 84$  meV. The region between 17 - 35 meV is dominated by two crystal-field peaks of the Nd ions, whose intensities go beyond the scale of the figure. The peak at 93 meV is also a crystal-field peak. **Figure 1(b).** GPDOS in  $(\text{Pr-Ce})_2\text{CuO}_4$ . Two crystal-field transitions are observed at 88 meV and 18 meV; the intensity of the 18 meV transition is 4400 counts. There are substantial changes in the peak intensities in the 30 - 58 meV region as the material changes from  $(\text{Nd-Ce})_2\text{CuO}_4$  to  $(\text{Pr-Ce})_2\text{CuO}_4$ .

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## ANTIFERROMAGNETIC ORDERING OF BaPrO<sub>3</sub>

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The superconducting properties of the layered perovskites RBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> (R123) change very little on substitution of the trivalent rare earth ion, R [1]. An important exception to this behavior is Pr, where the superconducting transition temperature decreases with increasing Pr concentration; superconductivity is completely suppressed for more than 60% Pr in the rare earth site [2]. Two proposed mechanisms exist to account for the suppression of superconductivity in Pr123: one suggests that the Pr is mixed-valent Pr<sup>3+</sup>/Pr<sup>4+</sup> where the electrons oxidized from Pr<sup>3+</sup> fill conduction band hole states [2]. The other suggests that there is hybridization between the Pr<sup>3+</sup> *f* shell and the conduction electrons [3]. In order to understand the behavior of Pr in Pr123, we are studying tetravalent Pr in BaPrO<sub>3</sub>, an orthorhombically-distorted perovskite which is a precursor to the more complicated layered-perovskite high-T<sub>c</sub> materials [4].

Reitveld refinements of T = 300, 17, and 5 K powder diffraction patterns of BaPrO<sub>3</sub> taken on BT-1 confirm that the structure is space group *Pbnm* as reported previously [5], with lattice parameters *a* = 6.2137 Å, *b* = 6.1787 Å, and *c* = 8.7261 Å. The Pr ions are surrounded by nearly symmetric oxygen octahedra, with Pr-O distances of 2.2252(6) Å along the *c* axis and 2.223(3) Å in the *ab* plane. The orthorhombic asymmetry is reversed from the previous incorrectly reported structural determination [5], with the present lattice parameter *a* approxi-

mately equal to the previously reported lattice parameter *b* and *vice versa*.

Diffraction scans at T = 5 K and 17 K were taken on BT-2 with λ = 2.3556 Å to study the magnetic order. Magnetic (difference) peaks appear at 2θ = 27(1)° and 53.0(1.4)° (fig. 1);

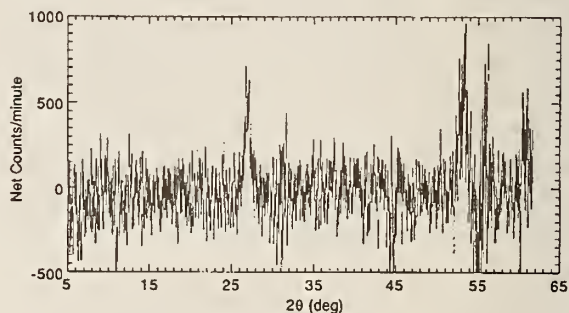


Figure 1. Difference between 2θ scans at T = 5 K and 17 K. Note the magnetic peaks at 2θ = 27(1)° and 53(1)° and the incomplete cancellation of the structural peak at 2θ = 55°.

difference peaks were also observed at 72(2)° and 89(2)°.

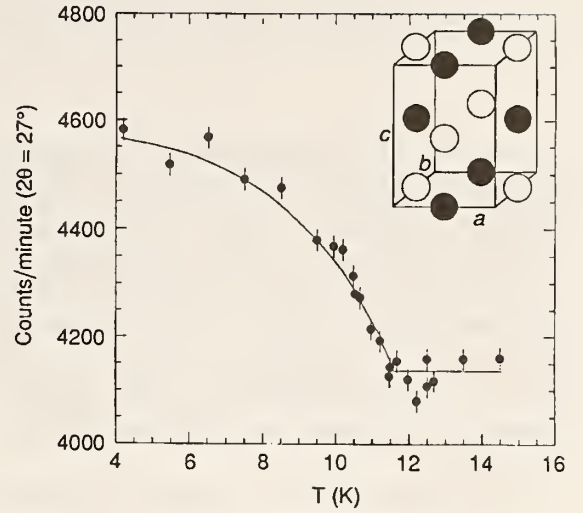
The temperature dependence of the 27° peak intensity (fig. 2) confirms that this peak is due to magnetic order with a Néel temperature T<sub>N</sub> = 11.7(2) K, in agreement with previous magnetic susceptibility, magnetization and specific heat measurements [4]. The magnetic reflections are coincident with nuclear Bragg peaks implying that the magnetic unit cell and structural unit cell are the same size. The spins are therefore staggered along the <110> and [001] directions. With the exception of the

$2\theta = 27^\circ$  peak, these difference peaks are approximately 1% of the intensity of the structural intensities at the same scattering angle.

Since the  $a$  and  $b$  axes of  $\text{BaPrO}_3$  differ by less than 1%, the spin direction can be determined with respect to the  $c$  axis, barring any accidental degeneracies. However,  $a \approx b \approx c/\sqrt{2}$  and so reflections for which  $2(h^2 + k^2) + l^2$  is a constant cannot be resolved in the present experiments. Thus all magnetic diffraction peaks are composed of reflections from many different directions in reciprocal space and the peak intensity ratios depend not on the spin direction but on the multiplicity of the contributing reflections.

The intensity ratios for the  $2\theta = 27^\circ$ ,  $53^\circ$ , and  $88^\circ$  reflections of 1:4.4(4):5.3(1.1) agree relatively well with the calculated multiplicity ratios of 1:3:4. Since the intensities do not depend on the spin direction, we can determine that the low temperature value of the moment is  $\langle \mu_z \rangle = 0.35(5) \mu_B$ . The expected saturated moment of  $\text{Pr}^{4+}$  is  $0.43 \mu_B$ , assuming a  $\pm 1/2$  doublet ground state of the crystal-field split  $^2F_{5/2}$  multiplet [3].

Since the magnetic and nuclear Bragg peaks occur at the same diffraction angles in this system, the technique of subtracting the high  $T$  data from the data at low  $T$  could in principle include both magnetic and nuclear components. Hence, the discrepancy between the observed difference intensity ratios and the intensity ratios expected on the basis of the multiplicity may be due in part to the inclusion of the effect of small structural changes in the nuclear peaks. In fact the uncertainty in the refined peak intensities, with the exception of the  $2\theta = 27^\circ$  peak, can be as large as one-half the observed difference intensity. As a result, it is impossible to distinguish between the small magnetic components and intensity differences due to small structural changes. In fact, the difference peak observed at  $2\theta = 72^\circ$  clearly has been significantly distorted by this effect. Further work will have to wait for suitable single crystals.



**Figure 2.** Temperature dependence of the  $2\theta = 27^\circ$  peak intensity, indicating  $T_N = 11.7(2)$  K. Inset: Antiferromagnetic ordering inferred from magnetic diffraction pattern, where the open circles indicate a spin pointing in some definite, undetermined, direction and the closed circles indicate a spin pointing antiparallel to that direction. The Pr moments are antiferromagnetically ordered along the  $\langle 110 \rangle$  and  $[001]$  directions.

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QUANTITATIVE DETERMINATION OF IMPURITY PHASES IN  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ 

J. K. Stalick

Neutron Rietveld refinement is a powerful technique in the study of high- $T_c$  superconductor powders, owing to the relative sensitivity of neutrons to oxygen content and the amenable powder line shape [1]. This method has been used as a tool for the detection and quantitative measurement of minor impurity phases in superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples, even when no resolved impurity peaks are evident.

Experimental neutron diffraction patterns were obtained for the common impurity phases  $\text{CuO}$ ,  $\text{Y}_2\text{BaCuO}_5$ ,  $\text{BaCO}_3$ , and  $\text{BaCuO}_2$ . The structures were refined to provide the best values for obtaining a calculated neutron pattern; however, the structure of  $\text{BaCuO}_2$  could not be completely refined owing to as yet unresolved difficulties in structure solution. High-resolution

powder diffraction data were then collected on a series of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples prepared under different processing conditions; the structures were refined, along with scale factors for the intensities of potential impurity phases which were included as a contribution to background.

The impurity phase commonly found was  $\text{CuO}$ , ranging in concentration from 17 wt. % (obvious) to 0.5(1) wt. %, which is not visually discernable in a plot of the data. In all cases the agreement factors  $\chi = R_{wp}/R_c$  and  $R_B$  improved statistically when the contributions of the impurity phase were included as part of the background calculation.

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NEUTRON POWDER DIFFRACTION STUDY OF THE NUCLEAR AND MAGNETIC STRUCTURES OF  $\text{YBa}_2\text{Fe}_3\text{O}_8$  AT ROOM TEMPERATURE

Q. Huang, A. D. Mighell, V. L. Karen, and A. Santoro

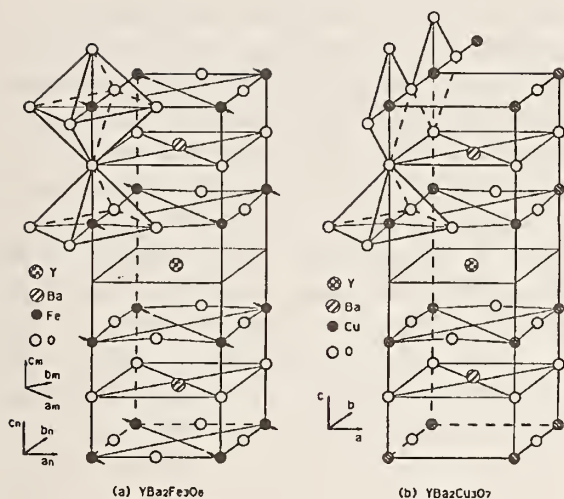
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and

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(University of Maryland, College Park, MD and Reactor Radiation Division)

The nuclear and magnetic structures of  $\text{YBa}_2\text{Fe}_3\text{O}_8$  have been investigated by powder neutron diffraction at room temperature. The nuclear structure of the compound has the symmetry of space group  $P4/mmm$  and lattice parameters  $a = 3.9170(1)$  and  $c = 11.8252(4)\text{\AA}$ . The configuration of the atoms in the unit cell is very similar to that of the superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , with the exception that the iron ions corresponding to the Cu chain ions have octahedral coordination, rather than square planar; the octahedra thus are arranged in layers rather than in chains. This significant difference is a consequence of the fact that all possible oxygen sites in these layers are fully occupied, resulting in an oxygen content of eight rather than seven atoms per formula unit. A second

consequence of the full occupancy of the oxygen sites is that the Ba ions have a twelvefold cuboctahedral coordination in the iron compound, rather than tenfold. The magnetic structure is based on a unit cell related to that of the nuclear structure by an axis transformation of matrix  $(1\bar{1}0/110/002)$ . The magnetic origin of the extra intensities and the basic spin configuration were determined by polarized neutron diffraction measurements. The iron moments are coupled antiferromagnetically within each  $\text{FeO}_2$  layer, as well as along the  $c$ -axis. The magnetic moments of all the iron ions are the same with a value of  $3.49(2)\mu_B$ . This configuration results in the magnetic symmetry  $I_{cmm}'m$ .



**Figure 1.** (a) Nuclear and magnetic structures of  $\text{YBa}_2\text{Fe}_3\text{O}_8$ . For simplicity, only the nuclear cell is shown in the figure. The magnetic cell is related to the nuclear one by the transformation of axes matrix  $(\bar{1} \ 1 \ 0/110/002)$ . The magnetic moments of the iron atoms lie in the planes perpendicular to  $c$ . Their direction in the plane, however, cannot be determined in our experiment and has been fixed arbitrarily along the  $a$ -axis of the magnetic cell. (b) Unit cell of the compound  $\text{YBa}_2\text{Cu}_3\text{O}_7$  shown for comparison with the iron compound.

## HAVE THE INTERMEDIATE BOSONS RESPONSIBLE FOR PAIRING IN THE HIGH-TEMPERATURE SUPERCONDUCTING COPPER-OXIDE MATERIALS BEEN FOUND?

R. C. Casella

For some time I have been considering models of high-temperature superconductivity in the layered copper-oxide compounds which involve the exchange of some heretofore unspecified high-energy ( $\omega \gg \omega$  (phonon)) intermediate bosons (IB) [1,2]. As discussed in the previous progress report [3], double IB exchange between pair constituents in one band via a third fermion in another band leads (when the IB and third fermion coordinates are integrated out) to effective pair correlations in each band. Moreover, the assumption that one band is associated with orbital overlap mainly in the  $ab$  planes while the other (very narrow) band (of width  $< 0(100 \text{ meV})$ ) is associated with the overlap of hybrid orbitals along  $c$  (i.e., between planes), led to a satisfactory explanation of the superconducting gap anisotropy observed in the compound  $\text{Bi}_2\text{SrCaCu}_2\text{O}_8$ . A basic assumption of the model is that interband scattering of the pair constituents via exchange of the IBs can be neglected. This assumption was originally introduced in an *ad hoc* way in order to maintain the identity of a given pair as belonging to one or the other of the two bands rather than

considering pairs with constituents, one from each of the two bands. It seemed rather natural within the context of the formalism but appeared somewhat mysterious, having no other physical basis, theoretical or experimental. Moreover, the nature of the IB remained a mystery, although in order to fit the model to the observed (anisotropic) tunneling gaps it is necessary to assume that the IB energy  $\omega > 0(0.3 \text{ eV})$ . *It now appears possible to link both mysteries and to understand them simultaneously. Moreover, it appears that an IB of comparable energy and similar origin has been found in the Y-123 system, suggesting further experimental tests of the model.*

Subsequent systematic examination of the infrared data for the Bi compound (keeping in mind that to be consistent with the tunneling data the model implies  $\omega > 0(0.3 \text{ eV})$ ) suggested identifying the broad infrared-active excitation centered at  $\approx 3000 \text{ cm}^{-1}$  [4] as a candidate IB. Since the IB couples to photons, it must possess nontrivial spectral density near  $\vec{q} = \vec{0}$ . But a large momentum transfer is required to scatter an approximately  $ab$ -moving fermion from near

the Fermi surface of the energetically wide quasi-two-dimensional ab band to an approximate c-mover in the energetically narrow c band. Hence, the identification of the high energy IB with a low-q excitation "justifies" *a posteriori* the neglect of interband scattering of the fermions at each stage of the double-IB exchange. The pair constituents ( $\vec{k}\uparrow, -\vec{k}\downarrow$ ) in a given band are indirectly coupled by the exchange of these high-E low-q IB's with the third fermion in the other band. At each stage the active pair constituent and the third fermion scatter very little but (virtually) exchange considerable energy. Two other remarks: (i) Large-q low-E phonons *can* lead to interband scattering between approximate ab- and c-movers, but this process presumably does not produce the high- $T_c$  condensate. (Such phonon-mediated interband transitions likely lead to *pair breaking* as  $T \rightarrow T_c$  from below.) (ii) Although not essential, the IB, if composite, might be an i.r.-active broad unbound electron-hole resonance, possibly accounting for the large width of the i.r. absorption. Thus the IB itself might be associated with a low-q interband transition of a fermion between two *other* energy bands in these complex high- $T_c$  systems.

Are there other experimental tests and can the model be applied to other high- $T_c$  crystals? The existence of a broad i.r.-coupled excitation in Y-123 centered at  $\approx 3300 \text{ cm}^{-1}$  [5] (or  $\approx 2100 \text{ cm}^{-1}$  [6]) suggests the latter may be true, if the reported tunneling-gap anisotropy can be confirmed. As to other tests, the high density of states associated with the narrow c band might be seen by angle-resolved photoemission on crystals oriented such that the component of  $\vec{k}$  along c is conserved, assuming sufficient energy resolution can be achieved. (I am aware only of angle-resolved work in which  $k_{ab}$  is conserved.) If such a peak shows up, it may still be difficult to disentangle it from one which would result from the high-mass component  $m_{cc}$  of a single anisotropic band. Nonetheless such studies would be useful. Returning to the i.r. experiments, the gap values for Y-123 as reported, e.g., in [7], have been the subject of controversy [4,5], quite apart from the disagreement with tunnel values. The i.r. detectability and even the existence of gaps in both the Y- and Bi-  $\text{CuO}_2$  systems have been questioned. (It is conceivable

that the gaps reported via interpretation of tunneling data are real, but not i.r. detectable, possibly due to the existence of states within the gaps.) I nevertheless consider the implications of the value  $2\Delta_{ab}/kT_c \approx 8$ , inferred from the i.r. data for Y-123 in [7] as well as elsewhere. Setting this ratio equal to 8.0 and setting  $\omega = 0.4 \text{ eV}$  (based upon our identification of the IB with the i.r. absorption centered at  $3300 \text{ cm}^{-1}$ ), the model then implies  $2\Delta_c/kT_c < 2.7$ . The prediction lies somewhat below the result  $2\Delta_c/kT_c \approx 3$ , inferred in [7]. The experimental situation requires clarification since the model predictions are unambiguous. If  $2\Delta_{ab}/kT_c = 8.0$ , then to obtain a value as large as 2.9 for the ratio  $2\Delta_c/kT_c$  within the model requires that  $\omega \approx 5 \text{ eV}$ , clearly at odds with our identification of the IB. (Table 1.)

Table 1. Computed values for the effective coupling  $g$ , intermediate boson cut-off energy  $\omega$ , narrow band width  $B_C$  and the parameter  $x_c^C = B_C/4kT_c$  for the Y-123 compound as a function of the ratio  $\omega/B_C = R/2$ , given that the critical temperature  $T_c = 92 \text{ K}$  and that the in-plane pair-excitation gap  $2\Delta_{ab} = 2\Delta_D = 63.4 \text{ meV}$ . Results are presented for four values of the parameter  $r = \Delta_D/\Delta_C = \Delta_{ab}/\Delta_c$  where  $2\Delta_c$  is the pair-excitation gap along the c-axis. (Data from [7].)

$\omega/B_C$	$g$	$\omega[\text{eV}]$	$B_C[\text{meV}]$	$x_c^C$
$r = 3.5 (2\Delta_c/kT_c = 2.3)$				
4	0.439	0.24	60.6	1.91
5	0.380	0.40	78.5	2.48
10	0.268	1.75	175	5.52
15	0.229	4.20	280	8.83
$r = 3.2 (2\Delta_c/kT_c = 2.5)$				
5	0.515	0.21	42.4	1.34
10	0.366	0.71	71.1	2.24
20	0.283	2.38	119	3.75
30	0.250	4.83	161	5.08
$r = 3.0 (2\Delta_c/kT_c = 2.7)$				
25	0.330	1.83	73	2.30
50	0.274	5.28	106	3.33
$r = 2.8 (2\Delta_c/kT_c = 2.9)$				
75	0.321	4.69	63	1.98
85	0.312	5.57	66	2.07

To conclude, I have examined in greater depth the *physical* ramifications of the high- $T_c$  modifications to the canonical two-band theory of superconductivity, which I introduced earlier [1]. The model has been applied to reported tunneling-gap anisotropies. This has led to identifying the observed broad i.r. absorptions at 0.3 eV to 0.4 eV in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  and in Y-123 as candidates for the exchanged IBs. This identification is consonant with our earlier assumptions, which seem to imply a two-stage pairing mechanism. Experimental tests have been proposed and the results submitted for publication [8].

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## STRUCTURAL STUDY OF $\alpha$ -FeCr NEAR THE $\sigma$ -PHASE TRANSITION

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and

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A single crystal of the binary alloy  $\alpha$ -Fe<sub>53</sub>Cr<sub>47</sub> was quenched to room temperature after annealing at 1108 K (5 K above the  $\sigma$ -phase transition for four days. The  $\alpha$ -phase, a body centered cubic solid solution, which exists over a wide temperature and concentration range may exhibit precursory structural fluctuations in the local atomic arrangements (i.e. short range order, local atomic arrangements) near the  $\sigma$ -phase equilibrium boundary.

X-ray synchrotron measurements of the diffuse scattering were made at beamline X-14 Oak Ridge National Laboratory (ORNL) at the National Synchrotron Light Source at Brookhaven National Laboratory. These data indicate a clustering tendency [1] (Fe-Fe and Cr-Cr nearest neighbors are more probable than Fe-Cr neighbors). Inverse Monte Carlo and Krivoglaz-Clapp-Moss determinations of pair interaction energies are self consistent and compare favorably with recent theoretical calculations [2]. The average individual Fe-Fe and Cr-Cr distances were also determined and reveal a contraction of both the Fe-Fe and the

Cr-Cr nearest neighbor distances. This result disagrees with a conventional treatment of atomic size effects in solid solutions and must be understood using species dependent solute-lattice couplings.

Elastic and inelastic neutron scattering measurements are currently under way to determine the more subtle structural features such as the static displacements which cannot be readily obtained from the X-ray measurements. A detailed analysis requires accurate values for the atomic force constants and the elastic constants. These were obtained by measuring the phonon dispersion curves (fig. 1) and fitting them to a 5 nearest neighbor Born-Von Karman model [3] and are listed in table 1. These measurements also provided an opportunity to search for soft modes indicating precursory  $\sigma$ -phase fluctuations (thus far none have been observed that cannot be attributed to other known effects in bcc crystals). Elastic diffuse neutron and Huang scattering measurements are planned in the near future.

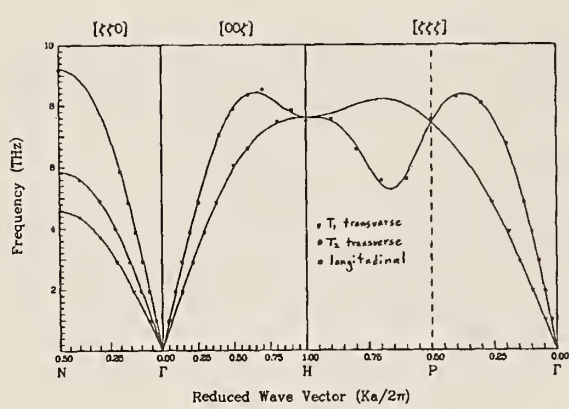


Figure 1. Phonon dispersion curves fit to a 5 nearest neighbor Born-Von Karman model.

Table 1. Atomic force constants in dynes/cm.

111	xx:13403	xy:13879			
200	xx:20105	yy: -376			
220	xx: 1442	zz: -744	xy: 634		
311	xx: -488	yy: -24	yz: -86	xy: -183	
222	xx: 971	xy: 1169			

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## COLLECTIVE EXCITATIONS OF LIQUID HELIUM IN RESTRICTED GEOMETRIES

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S. K. Satija

The effects of restricted geometries on the properties of liquid  $^4\text{He}$  have generated considerable experimental and theoretical interest recently. Of particular interest [1] has been the effect of confinement and random surface potentials on the properties of the superfluid phase. Measurements [2] have been carried out in porous glasses such as vycor, aerogel, and xerogel and a variety of effects have been observed. In vycor, which has a small and relatively uniform pore size distribution, the superfluid transition is substantially suppressed, but the critical exponent for the superfluid density is not measurably changed. Alternately, in aerogel, which has a much more open structure and a wide range of characteristic pore sizes, little suppression of the superfluid transition is observed. However, the critical exponent is substantially different from the bulk liquid case, which indicates that this systems may belong to a different universality class.

Previous studies have concentrated primarily on the macroscopic properties of the confined liquid such as the heat capacity and superfluid fraction [2]. However, there has been little work on the effects of the confining geometry on

the microscopic properties of the liquid. Therefore, we have undertaken a study of the collective excitations of superfluid helium confined in aerogel glass using inelastic neutron scattering.

The confining medium used for these studies was a highly porous aerogel glass. The glass had a porosity of  $\sim 95\%$  and consists of highly interconnected pores with sizes ranging from 10s to 1000s of angstroms. Aerogel glass was used so that a large amount of helium could be placed in the pores allowing a good signal to noise ratio to be obtained for the confined liquid. Previous measurements have shown that the superfluid transition temperature is only slightly depressed by confinement in the aerogel but that the critical exponents for the superfluid transition are significantly modified.

The measurements were carried out using the BT-2 and BT-4 spectrometers with an incident energy of 5 meV. Data were collected on both bulk liquid helium and helium in aerogel for momentum transfers between  $0.4$  and  $2.3 \text{ \AA}^{-1}$ , covering the phonon, maxon, and roton regimes. The collective excitations of the bulk liquid at low temperatures are very sharp and

provide a measure of the instrumental resolution. The temperature dependence of the helium in aerogel was also measured for temperatures between 1.4 and 2.1 K.

The collective excitation spectrum in bulk superfluid helium exhibits a sharp response over a broad range of momentum transfer,  $Q$ , that is unlike that observed in conventional liquids [3]. The collective excitation spectrum can be divided into three different regions. At low  $Q$ , the collective excitations are phonons and the energy is very nearly linearly, proportion to  $Q$ . At intermediate  $Q$  the collective excitation spectrum shows a peak known as the maxon. At larger  $Q$ 's the dispersion relation shows the characteristic dip associated with the roton.

The energy of the collective excitations was measured in both the bulk and confined superfluids for several  $Q$ 's at 1.5 K. Within the statistical accuracy of the measurements there was no difference in the energies of the collective excitations. However, the widths of the excitations are substantially different. Figure 1 shows the widths of the collective excitation for bulk He and He in aerogel. In bulk He, the excitation is very sharp and provides a measure of the instrumental resolution. The widths for He in aerogel, as seen in the figure, are systematically larger than for the bulk.

The finite width of the excitations of the confined liquid can be qualitatively understood. In the bulk liquid the width is due to excitation-excitation scattering and, at low temperatures, is very small. However, for the confined liquid an additional method for broadening the excitations exists--scattering from the walls of the aerogel. This simple picture also provides, again qualitatively, the correct  $Q$  dependence for the broadening. The phonons, which are long wavelength excitations, are more sensitive to the walls and are broadened much more than the rotons, which are thought to be highly localized excitations.

The temperature dependence of the broadening is also of interest since this provides information on the scattering of excitations. Figure 2 shows the temperature dependence for the roton ( $Q = 1.9 \text{ \AA}^{-1}$ ) for the helium in the aerogel and for the bulk liquid. In the bulk, the increase in width with temperature is due to the thermal excitation of the collective excitations.

This mechanism will also be present in the confined liquid. At  $\sim 2 \text{ K}$  the widths for the confined and bulk superfluids become comparable indicating that thermal broadening is the dominant feature at this temperature.

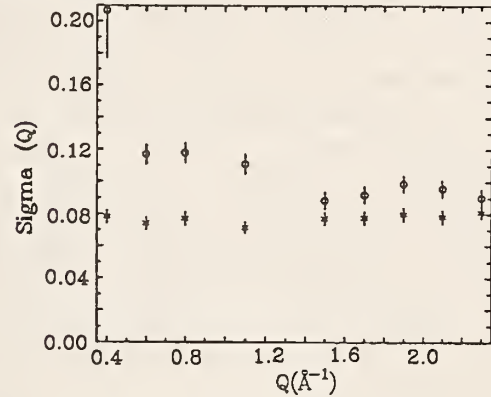


Figure 1. The width of the collective excitation peak as a function of momentum transfer at a temperature of 1.5 K. The stars are the results for the bulk liquid. At this temperature the true width of the excitations is vanishingly small and these results give the instrumental broadening for the spectrometer. The open circles are the results for liquid helium in aerogel glass. The peaks are significantly broader than the instrumental resolution due to the effects of the aerogel on the liquid.

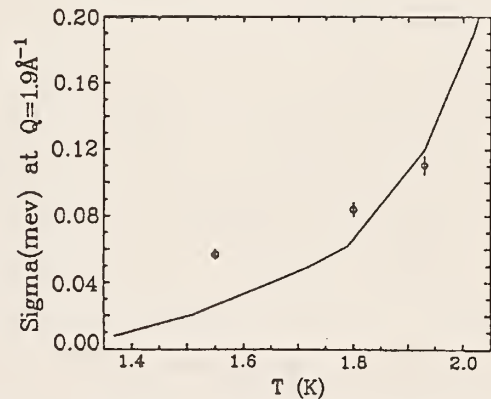


Figure 2. The open circles show the temperature variation of the width of the roton peak ( $Q = 1.9 \text{ \AA}^{-1}$  instrumental broadening). The solid line is the temperature variation in the bulk liquid.

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TOWARD NON-GAUSSIAN RANDOM MODELS OF SURFACE ROUGHNESS FOR  
NEUTRON AND X-RAY REFLECTIVITY

N. F. Berk

Most theoretical treatments of surface roughness in neutron and x-ray reflectivity studies assume that the surface height function  $z(r_2)$ , where  $r_2$  is the transverse position vector, is a Gaussian random function [1]. This is mathematically convenient but possibly restrictive in the scope of physical models of roughness it actually encompasses. We are interested in extending the analysis of surface sensitive scattering to non-Gaussian roughness models and have begun by devising a particular class of models that is amenable to some degree of exact treatment.

We note to begin with that in the Born approximation, valid not too close to the critical angle, the scattered (reflected) intensity depends on the surface height function according to

$$I(Q) = \frac{A}{Q_z^2} \int \exp(iQ_2 \cdot r_2) \quad (1)$$

$$\langle \exp\{iQ_z [z(r_2) - z(O_2)]\} \rangle > d^2r_2$$

where  $A$  is a constant. We are considering a random terrace model for  $z(r_2)$  in the form

$$z(r_2) = \frac{\sqrt{2}h}{\sqrt{J}} \sum_{j=1}^{2J} \zeta_j[z(r_2)], \quad (2)$$

where the  $\zeta_j$  in (2) represent independent samples of a random step function,  $\zeta(r_2) = \pm 1/2$ . Thus the sum in (2) takes on the  $M = 2J + 1$  values  $J, J - 1, \dots, -J$ , for  $J = 1/2, 1, \dots$ . Also,  $\langle z(r_2) \rangle = 0$  and  $\langle z(r_2)^2 \rangle = h^2$ . In the limit  $J \rightarrow \infty$  the model for  $z(r_2)$  tends to a Gaussian random function, for then at each  $r_2$  it is an infinite sum of random variables to which the central limit theorem applies. In this case, as for any Gaussian random variable with zero mean,

$$\langle \exp\{iQ_z [z(r_2) - z(O_2)]\} \rangle = \exp\left\{-\frac{1}{2} Q_z^2 \langle [z(r_2) - z(O_2)]^2 \rangle\right\}, \quad (3)$$

where, in the given model,

$$\langle [z(r_2) - z(O_2)]^2 \rangle = 2h^2[1 - \gamma(r_2)], \quad (4)$$

with

$$\gamma(r_2) = 4 \langle \zeta(r_2) \zeta(O_2) \rangle, \quad (5)$$

and  $\gamma(O_2) = 1$ . For finite  $J$ , however, the model  $z(r_2)$  is not a Gaussian random function, and the cumulant expansion implicit in (3) does not truncate. Nevertheless, we have derived an exact expression for the right hand side of (3). Indeed, if we define

$$F_J(r_2) = \langle \exp\left\{i \frac{\sqrt{2} Q_z h}{\sqrt{J}} \sum_{j=1}^{2J} [\zeta_j(r_2) - \zeta_j(O_2)]\right\} \rangle, \quad (6)$$

then, under the conditions of the model,

$$F_J(r_2) = \{1 - \sin^2(Q_z h / \sqrt{2J}) [1 - \zeta(r_2)]\}^{2J}. \quad (7)$$

Using a standard limit, we have almost at once from (7) that

$$\lim_{J \rightarrow \infty} F_J(r_2) = \exp\{-Q_z^2 h^2 [1 - \gamma(r_2)]\}, \quad (8)$$

which retrieves the correct result for a Gaussian random height function, as seen from (3) and (4).

From (1) the scattered intensity is

$$I(Q) = \frac{A}{Q_z^2} \int \exp(iQ_2 \cdot r_2) F_J(r_2) d^2r_2. \quad (9)$$

The specular contribution to the intensity is defined by the limit of  $F_J(r_2)$  as  $r_2 \rightarrow \infty$ . Thus from (7), assuming  $\gamma(r_2) \rightarrow 0$  in the limit, we have

$$I_{spec}(Q) = \frac{(2\pi)^2 A}{Q_z^2} \cos^{4J}(Q_z h / \sqrt{2J}) \delta(Q_z). \quad (10)$$

Compare this to the Gaussian model, for which

$$I_{spec}(Q) = \frac{(2\pi)^2 A}{Q_z^2} e^{-Q_z^2 h^2} \delta(Q_z). \quad (11)$$

Thus for finite, not too large, values of  $J$ , the specular scattering from the random terrace surface oscillates strongly with  $Q_z$ . Moreover, the non-specular scattering will also vary strongly with  $Q_z$  and have generally complicated line shapes as a function of the transverse wavevector  $Q_2$ .

Up to this point we have not had to specify a particular model for the random step function,  $\zeta(r_2)$ . One possibly useful class of such functions is a 2-d analogue of the leveled wave construction developed originally for random 3-d structures [2,3]. Thus let

$$\zeta(r_2) = \theta[S(r)] - \frac{1}{2}, \quad (12)$$

where  $\theta(x)$  is the Heaviside function and

$$S(r) = \frac{1}{\sqrt{N}} \sum_{n=1}^N \cos(k_{2n} \cdot r_2 + \phi_n). \quad (13)$$

The indexed quantities in (13) are independent random variables. The phase constants  $\phi$  are uniformly distributed in  $(0, 2\pi)$  for homogeneity, while the directions of  $k_2$  are distributed according to the degree of isotropy required of the terraces. For example, totally isotropic terraces correspond to a uniform distribution of  $k_2$ -directions. The magnitudes of  $k_2$  are distributed with probability density  $P(k_2)$ .

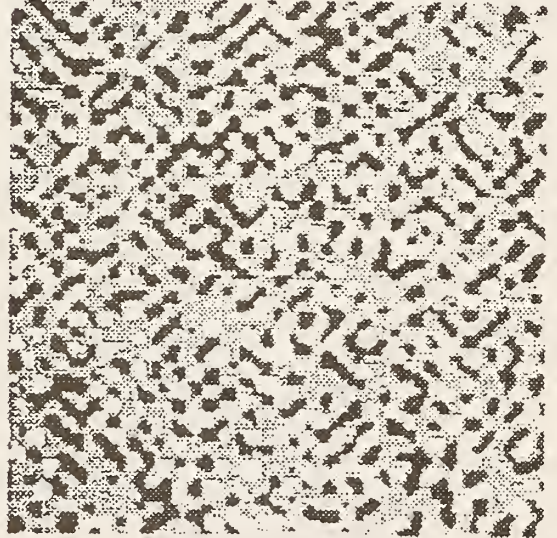
Thus, using the formalism already in place for the 3-d leveled wave method [2], we get

$$\gamma(r_2) = \frac{2}{\pi} \arcsin[\tau(r_2)], \quad (14)$$

where

$$\tau(r_2) = \int_0^\infty J_0(k_2) P(k_2) dk_2. \quad (15)$$

this scheme, then, analysis of non-specular scattering provides information about the model distribution function,  $P(k_2)$ . Figure 1 shows an example of a leveled wave terrace for  $J = 1$ , corresponding to  $M = 3$  distinct surface levels. We are currently developing the leveled wave random terrace model for application to reflectivity data from real surfaces. Extensions to scattering from multilayers are also planned.



**Figure 1.** Computer simulation of leveled wave, isotropic random terrace for  $J = 1$ . The three levels are indicated by white (level 1), grey (level 0) and black (level -1).

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# THEORY OF FRACTAL BEHAVIOR IN THE LEVELED WAVE MODEL OF RANDOM MORPHOLOGIES

N. F. Berk

The leveled wave model of random bicontinuous morphologies has been extended to fractal structures. Beyond the mathematical interest of the technique, it may be relevant to the observed deviations from Porod's law in small angle scattering experiments on various porous glass systems which usually are attributed to fractal roughness. A model that adds fractal roughness to the surfaces of a bicontinuous structure in a geometrically consistent way has been lacking up to now.

In the leveled wave scheme of random morphologies [1], continuous interfaces are mathematically modeled by level sets—2-d contours—of a stochastic standing wave,  $S(r)$ , which is defined by

$$S(r) = \frac{1}{\sqrt{N\langle A^2 \rangle}} \sum_{n=1}^N \cos(k_n \cdot r + \phi_n) \quad (1)$$

where the subscripted quantities on the right are taken to be independent random variables. A corresponding density function,  $\rho(r)$ , can be defined pointwise by  $\rho(r) = 1$  or  $\rho(r) = 0$ , say, according to whether  $S(r) > \beta$  or  $S(r) < \beta$ , respectively. One way of writing this is

$$\rho(r) = \Theta(S(r) - \beta), \quad (2)$$

where  $\Theta(x)$  is the Heaviside function:  $\Theta(x) = 1$  for  $x \geq 0$ , and 0, otherwise. The phase constants,  $\phi_n$ , are chosen from a uniform distribution over  $(0, 2\pi)$ . This makes  $S(r)$  spatially homogeneous; no special value of  $r$ , including the origin, is singled out. For an isotropic morphology, the directions of the random wavevectors,  $k_n$ , are uniformly distributed over solid angle  $4\pi$ . All other properties of the construction are then determined by the distribution,  $P(k)$ , of the magnitudes of  $k_n$  which is normalized by

$$\int_0^\infty P(k) dk = 1 \quad (3)$$

Scattering from the morphology is obtained from

$$I(Q) = 4\pi V c(1 - c) \int_0^\infty r^2 \gamma(r) j_0(Qr) dr, \quad (4)$$

where  $c = (1 - \text{erf}(\beta))/2$  and  $\gamma(r)$  is the Porod-Debye correlation function,

$$c(1 - c)\gamma(r) = c^2 - \langle \rho(r)\rho(0) \rangle. \quad (5)$$

The mathematical properties of this model have been developed in detail [1, 2]. In particular, the surface-to-volume ratio of the interface is proportional to the second moment of  $P(k)$ , indicating that sufficiently long-tailed  $k$ -distributions generate very rough surfaces, including those which are fractal [2]. To develop this idea analytically we considered that  $P(k)$  was contained in the convex family of functions

$$P(k) = [1 - \mu(\epsilon)]P_{st}(k) + \mu(\epsilon)P_{lt}(k), \quad (6)$$

where  $\mu(\epsilon) \in [0, 1]$ . We treat  $P_{st}(k)$  as a short-tailed function possessing all moments, and  $P_{lt}(k)$  as a long-tailed function which behaves asymptotically ( $k \rightarrow \infty$ ) the same as

$$P_{lt}(k) = \frac{2\ell_0\epsilon}{(1 + k\ell_0)^{(2\epsilon+1)}}, \quad (7)$$

where  $\ell_0$  is a fixed but arbitrary length and

$$\epsilon = 3 - D, \quad 2 < D < 3, \quad (8)$$

is the codimension of the fractal dimension,  $D$ . The long tail of  $P_{lt}(k)$ , weighted by the mixing parameter  $\mu(\epsilon)$ , provides the mechanism for fractal behavior. We require that both  $P_{st}(k)$  and  $P_{lt}(k)$  are normalized so that  $P(k)$  is normalized for all functions in this set. The asymptotic behavior of  $P(k)$  ultimately fixes the asymptotic law of the scattering. Specifically, we have found that for  $Q\ell_0 \gg 1$ ,

$$I(Q) \sim A(\epsilon)Q^{-\epsilon-3} \quad Q \rightarrow \infty, \quad (9)$$

corresponding the Bale and Schmidt "6 - D" law for scattering from fractal surfaces, where, for  $\beta = 0$ , the proportionality is given by

$$A(\epsilon) = \frac{2\sqrt{2}(\epsilon + 1)}{\pi^2 \sqrt{2\epsilon!}} \sqrt{2\epsilon \mu(\epsilon) l_0^{2\epsilon} \tan\left(\frac{\pi\epsilon}{2}\right)}. \quad (10)$$

The behavior of the square root in (10) at the Euclidean limits,  $D \rightarrow 2$  and  $D \rightarrow 3$ , requires discussion. First, the tangent diverges as  $\epsilon \rightarrow 1$ , which can be interpreted as expressing the implicit discontinuity in the moment expansion of long-tailed functions. The second moment,  $\langle k^2 \rangle$ , does not exist for functions acting as  $P_{lt}(k)$  when  $\epsilon < 1$ , but it is finite if  $\epsilon > 1$  is allowed. Thus, for the scattering to be finite at  $D = 2$ , we require  $\mu(\epsilon) \rightarrow 0$  at least as fast as  $1 - \epsilon$  as  $\epsilon \rightarrow 1$  and that  $\mu(\epsilon) = 0$  for  $\epsilon \geq 1$ . Then

$$A(1) = \frac{2l_0}{\pi^3} \sqrt{|\mu'(1)|}, \quad (11)$$

where  $\mu'$  is the derivative of  $\mu$ .

The nature of fractal scattering for  $D \rightarrow 3$  ( $\epsilon \rightarrow 0$ ) is also subtle and in other contexts has been subject to interesting debate. The basic issues are: according to (10), the (leading) asymptotic scattering from a "surface" fractal vanishes identically as  $D \rightarrow 3$ , rather than approaching the finite  $Q^{-3}$  dependence expected for scattering from a "volume" fractal; and if the leading  $Q^{-3}$  scattering does indeed vanish, then what is the mathematical nature of the asymptotic scattering? The leveled wave method follows a scenario in which the structure, while space-filling in the limit, nonetheless retains its topological character as an interface. The asymptotic scattering vanishes because the contrast between the two sides of the interface effectively disappears in the limit. For the second point it has been argued that the leading order nonvanishing scattering in the  $D = 3$  limit should be  $Q^{-4}$  scattering associated with the "ordinary" length scale of the porous structure.

To deal with this question in the leveled wave model, it is necessary to extend the expansion in (10). We have found that

$$I(Q) < \frac{\sqrt{2} l_0^{3\epsilon}}{(Ql_0)^3 \sqrt{(Ql_0)^{2\epsilon} + \frac{1}{2}}}, \quad (12)$$

for  $Ql_0 \rightarrow \infty$  and  $\epsilon \rightarrow 0$ . Thus at  $D = 3$  the right hand side of (12) vanishes as  $O(\epsilon)$ , and the scattering from the leveled wave morphology falls faster than algebraically (*i.e.*, exponentially) as  $Q \rightarrow \infty$ . Near  $D = 3$  the large- $Q$  scattering falls algebraically but not as a well-isolated power law.

In the leveled wave model, therefore, there is no evidence in the *asymptotic* scattering of nonfractal length scales, even though such scales are implicit in the structure from  $P_{st}(k)$  and will contribute structure to the scattering at small  $Q$ .

Leveled wave "fractal" structure, seen as a planar slice through the 3-d image, is shown in figure 1. For this computer simulation, the short-tailed component of the  $k$ -distribution has the form,  $P_{st}(k) = \delta(k - k_0)$ , where  $k_0$  determines the overall scale, and the long-tailed component is given by (7) with  $D = 2.5$ .

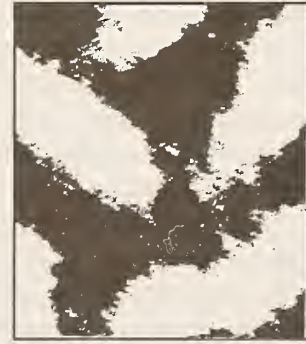


Figure 1. Computer simulation of leveled wave fractal pores for  $D = 2.5$  and 50% porosity.

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THEORY OF COHERENT NEUTRON SCATTERING FROM  $n$  ITINERANT SCATTERERS EMBEDDED IN CRYSTAL LATTICES

R. C. Casella

Some years ago, in an attempt to understand the rather large widths reported by Rush et al. [1] and Magerl et al. [2] for the peaks associated with the inelastic scattering of neutrons from dilute hydrogen atoms in the bcc metals Nb, Ta, and V, I was led to consider the possibility that the neutrons scatter from hydrogen atoms, which (in the excited-oscillator final state) move in protonic energy bands [3]. These bands are analogous to, but generally much narrower than, the electronic energy bands which typically occur in solids. Their essential feature is that the phase of the proton wave function remains coherent as the (shielded) proton (or modified hydrogen atom) traverses several interstitial sites, whence its wave function (in the excited-oscillator state) is Bloch-like (although possibly modified by incoherent lifetime effects [4]). Such (limited) phase coherence plays a role in this theory, even when the neutron scatters from a single itinerant proton. In contrast, when a neutron scatters from more than one hydrogen (be they quasi-localized or itinerant) the average over initial spin states of the hydrogens leads to well-known spin incoherence. That is, the cross section for a neutron to scatter from  $n$  hydrogens is essentially  $n$  times the average cross section for it to scatter from only one, even for the case when the neutron scatters elastically from hydrogens, each of which, for a given spin, is in a spatially (quasi) coherent Bloch-like state. What happens when the spin incoherence is not a factor as would be the case in the elastic scattering of a neutron from  $n$  itinerant deuterium atoms, where the overlap between the deuterium oscillator

wave functions sufficient to produce Bloch-like phase coherence in the individual deuterium wave functions even in the ground state? It has recently been claimed in the literature that a factor  $n^2$  enters in the cross section for processes such as this. I believe this result is incorrect, except for the very special case where the  $n$  scatterers are confined within a volume of linear dimensions each  $< O(\lambda)$  where  $\lambda$  is the wavelength of the incoming neutron. My belief is based, in part, on my earlier work on the distinct but somewhat analogous situation involving the possibility of coherent scattering of reactor-generated neutrinos from  $N$  quasi-localized atomic nuclei in crystal materials. I showed then that, as in the well-known case of Bragg scattering of neutrons from crystals, the cross section for coherent neutrino scattering is proportional to  $N$  rather than  $N^2$  [5,6], contrary to the  $N^2$  behavior claimed in the literature at the time. I plan to demonstrate analytically that, in the present case, the neutron cross section is proportional to  $n$ , not  $n^2$ .

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## B. CHEMICAL PHYSICS AND CRYSTALLOGRAPHY

The work described in these areas generally relates to materials whose primary interest or functionality is chemical. The diversity of systems investigated by neutron scattering and crystallographic techniques continues to grow. Neutron scattering group scientists, in cooperation with U. Penn, Penn State and Exxon, have carried out the first elastic and inelastic scattering studies of buckminster fullerene, which have revealed critical information on the dynamics, orientational disorder and rotator phase transition in this fascinating new molecular architecture. Our longstanding research efforts in layered materials, catalysts and hydrogen in metals have

during the past year yielded interesting new results, for example, on hydrogen potentials and dynamics in rare earth and refractory metal-hydrogen systems and on the dynamics and structure of boron nitride and of new molecular complexes in intercalated graphite. Important progress has been made in the extension of maximum entropy methods and related fast Fourier transform codes for macromolecular phase determination. Studies have also been extended to systematic investigations of the dynamics of glasses and aerogels, to the structure of Langmuir Blodgett multilayers and to the structure and flow of colloidal suspensions under shear.

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### OBSERVATION OF C-AXIS MODE-SPLITTING IN $\alpha$ -LuH<sub>0.19</sub>

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In recent years, we have investigated, by incoherent inelastic neutron scattering (IINS), the structure and dynamics of hydrogen in two rare-earth hcp metals, Y and Sc, that form  $\alpha$ -phase solid solutions. As mentioned in this report on p. 56, although hydrogen occupies tetrahedral interstices (i.e., t sites) in these metal host lattices, IINS investigations have indicated that an anharmonic, anisotropic soft mode exists for vibrations polarized along the c-axis, 25-30% lower in energy than the doubly-degenerate basal-plane modes. Moreover, this c-axis mode possesses a spectral lineshape that is much broader than the instrumental resolution, and for high H concentrations and low temperatures, is distinctly split into two components. This splitting is caused by hydrogen pairs dynamically coupled across metal atoms along the c-axis.

To make a more thorough comparison of hydrogen dynamics in rare earth metals, an investigation was undertaken of hydrogen in Lu, namely,  $\alpha$ -LuH<sub>0.19</sub>, which lies very close to the  $\alpha$ -LuH<sub>x</sub>/ $\beta$ -LuH<sub>2</sub> phase boundary. Previous

work on  $\alpha$ -LuD<sub>0.19</sub> [1] has suggested a very unusual, large ( $\sim 8$  meV) splitting for the c-axis-polarized D vibration. In the present work, spectra were measured with the BT-4 spectrometer using both the Be-filter (low-resolution) and Be-graphite-Be filter (high-resolution) analyzers. Low-resolution H vibrational spectra establish the c-axis and basal-plane mode energies at 102.5 and 144 meV, respectively, and a ratio of 1.78 for the second- to first-excited-state energies of the c-axis vibration, again verifying the anisotropy and anharmonicity of the rare-earth t-site potential along the c-axis. Figure 1 shows high-resolution IINS spectra of the c-axis vibration as a function of temperature. In agreement with the other rare-earth studies, the c-axis peak possesses a broad multicomponent lineshape indicating hydrogen-pairing-induced splitting at low temperature. As the temperature is increased, this splitting disappears, suggestive of increased H disorder within the metal lattice. Figure 2 compares the low-temperature c-axis

spectra for the three investigated H/rare-earth  $\alpha$ -phases in the order of decreasing lattice constant  $c$  from Y (0.573 nm) to Lu (0.555 nm) to Sc (0.527 nm). Proceeding from Y to Sc, the overall lineshape becomes broader and the splitting becomes less distinct, consistent with decreasing H-pair order as the lattice constant  $c$  decreases. Further isotope and concentration-dependent studies are under way for this system.

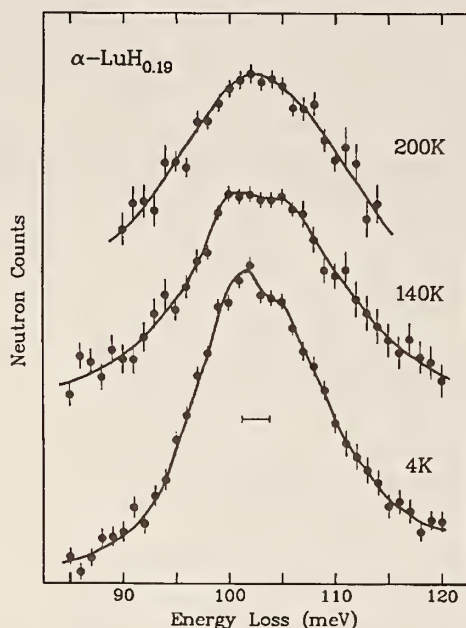


Figure 1. High-resolution IINS spectra of the c-axis mode for  $\alpha$ -LuH<sub>0.19</sub> as a function of temperature. Solid lines are drawn to guide the eye. The instrumental resolution (fwhm) is illustrated by the horizontal bar beneath the spectra.

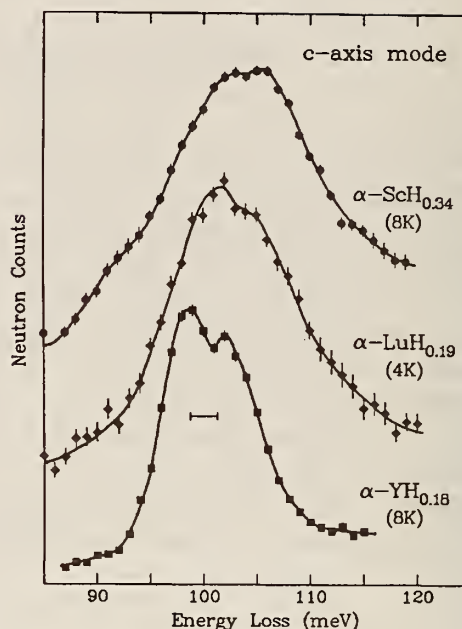


Figure 2. A comparison of high-resolution IINS spectra below 10 K of the H c-axis mode for Y, Sc, and Lu high-H-concentration  $\alpha$ -phases. Solid lines are drawn to guide the eye. The instrumental resolution (fwhm) is illustrated by the horizontal bar beneath the spectra.

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## QUANTUM HOPPING OF PROTONS IN $\alpha$ -ScH<sub>x</sub> AND $\alpha$ -YH<sub>x</sub>

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We are continuing our studies of local hydrogen dynamics in rare earth metals using quasielastic neutron scattering. Previously [1] we had measured a striking minimum in the proton hopping rate near  $T = 100$  K in ScH<sub>0.15</sub>, the first such observation in a pure metal-hydrogen system. In addition, the hopping rate at lower temperatures, which approaches  $10^{12} \text{ s}^{-1}$  near  $T = 10$  K, is faster than any previously seen in such systems. We have extended these

measurements to several concentrations of hydrogen in scandium and have also measured quasielastic scattering from low concentrations of hydrogen in yttrium. The quasielastic line widths for these measurements are collected in figure 1. The previous data for ScH<sub>0.15</sub> are also shown. A minimum quasielastic linewidth and "hopping" rate near  $T = 100$  K is clearly evident at both the lower and higher concentrations of hydrogen in scandium. Figure 1 also

presents linewidth data for  $\text{YH}_{0.01}$ , which also shows a definite minimum near  $T = 150$  K and at somewhat slower local hopping rate than observed for the  $\text{ScH}_x$  alloys. The combined evidence in figure 1 indicates the phenomenon of the hopping rate minimum is generic in these systems.

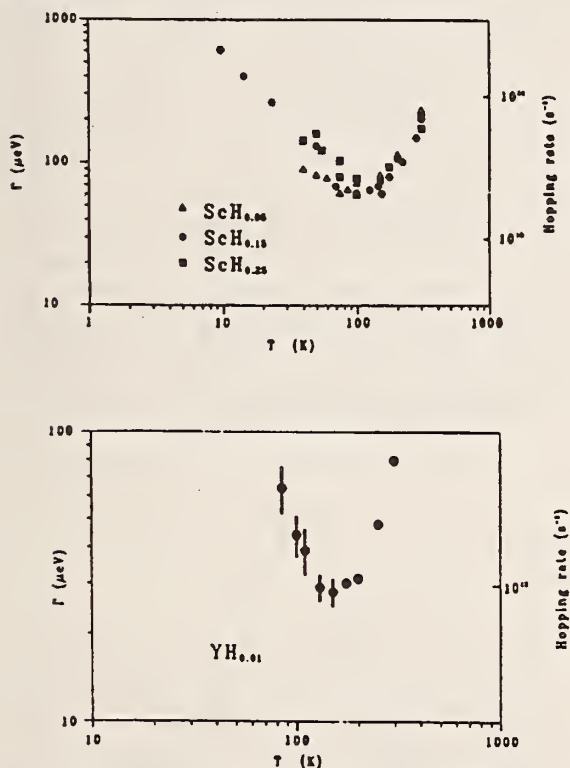


Figure 1. Quasielastic neutron scattering linewidth  $\Gamma$  vs  $T$ . Top:  $\alpha\text{ScH}_x$  for  $x = 0.05, 0.15$ , and  $0.25$ , Bottom:  $\alpha\text{-YH}_x$  for  $x = 0.01$ .

As described elsewhere [1,2], we have attributed the anomalous temperature dependence of the hopping rate to coupling of the interstitial protons to the metal conduction electrons, as originally developed theoretically by Kondo and others. These non-classical effects on the motion are amplified in the rare-earth metals for those "labile" protons able to hop rapidly back and forth between nearest neighbor tetrahedral sites along the  $c$ -axis of the hcp metal lattice. At low temperatures, in our picture, most of the protons, in fact are rendered "non-labile" on the time scale of the measurement because of coherent strain interactions that produce strong short range order. The population of the labile species that exhibits the anomalous hopping thus

decreases rapidly as temperature decreases. In our model the labile and non-labile populations are energetically operated by an effective binding energy. This energy can be inferred from the temperature dependence of the elastic component of the quasielastic measurement, known as the EISF or elastic incoherent structure factor. In figure 2 we show model fits to the measured EISF from  $\text{YH}_x$  for  $x = 0.01$  and  $x = 0.1$ . These fits determine short ranged ordering energies of approximately 50 meV, which is consistent with independent estimation of "pairing" energies in the systems from analysis of thermodynamic measurements.

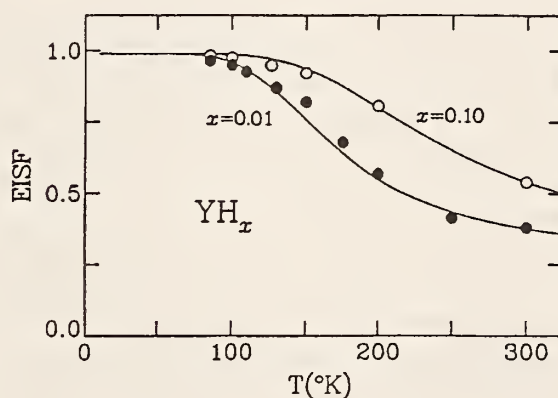


Figure 2. Elastic incoherent structure factor EISF vs  $T$  for  $\alpha\text{-YH}_x$  with  $x = 0.01$  and  $x = 0.1$ . The solid line is a fit to a model in which labile and non-labile proton populations are separated in energy by  $\sim 50$  meV.

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VIBRATIONAL MODES AND LINESHAPES IN  $\alpha$ -ScH<sub>0.34</sub> and  $\alpha$ -ScD<sub>0.34</sub>T. J. Udovic, J. J. Rush, and N. F. Berk  
and

I. S. Anderson (Paul Scherrer Institut, Villigen, Switzerland)

In  $\alpha$ -ScH<sub>x</sub> ( $x_{\text{max}} \sim 0.35$ ) solid solutions, hydrogen occupies the tetrahedral interstices (i.e., t sites) of the Sc metal lattice. Previous studies of  $\alpha$ -ScH<sub>x</sub> at H concentrations  $x \leq 0.25$  [1] have indicated that the H vibration along the c-axis direction (at ca. 103 meV) is over 30% lower in energy than the doubly-degenerate basal-plane modes (at ca. 148 meV) and possesses considerable anharmonicity, as reflected by the ratio (1.76) of the second- to first-excited-state energies. High-resolution neutron spectra for the c-axis vibrations revealed a peak at all hydrogen concentrations that was much broader (ca. 14 meV full width half maximum intrinsic linewidth,  $x = 0.25$ ) than the instrumental resolution, yet devoid of any resolved fine structure indicative of a distinct local-mode splitting due to the dynamic coupling of hydrogens paired across Sc atoms along the c-axis as was observed previously for  $\alpha$ -YH<sub>x</sub> [2]. Although the broad overall widths of the  $\alpha$ -ScH<sub>x</sub> c-axis peaks at these H concentrations were consistent with the presence of H pairing across Sc atoms along the c-axis at low temperatures, the lack of a distinct splitting suggested that the ordering of the hydrogen pairs themselves along the c-axis was less extensive than in  $\alpha$ -YH<sub>x</sub>.

Recently, the H(D) vibrational spectra of  $\alpha$ -ScH<sub>0.34</sub> and  $\alpha$ -ScD<sub>0.34</sub> have been measured using incoherent inelastic neutron scattering (IINS) methods in order to further characterize the bonding potential of H(D) in the t sites very close to the  $\alpha$ -ScH(D)<sub>x</sub>/β-ScH(D)<sub>2</sub> phase boundary. Spectra were measured with the BT-4 spectrometer using both the Be-filter (low-resolution) and Be-graphite-Be-filter (high-resolution) analyzers. Low-resolution H(D) vibrational spectra locate the c-axis mode energies at 103.5(78.5) meV and the basal-plane mode energies at 147.5(106.8) meV. Figure 1 illustrates the high-resolution c-axis vibrational

spectrum for  $\alpha$ -ScH<sub>0.34</sub> compared with that for  $\alpha$ -ScH<sub>0.25</sub> and  $\alpha$ -YH<sub>0.18</sub>. In effect, increasing the H concentration has led to a more fully developed ordering of hydrogen pairs along the c-axis as indicated by the growth of scattering intensity on the higher-energy side of the c-axis peak, leading to the emergence of a faint local-mode splitting of ca. 4-5 meV, similar to that found for  $\alpha$ -YH<sub>0.18</sub>. Figure 2 illustrates the high-resolution c-axis vibrational spectrum for  $\alpha$ -ScD<sub>0.34</sub>. The shape of this spectrum suggests the presence of a broad multicomponent feature and is consistent with the results for  $\alpha$ -ScH<sub>0.34</sub>.

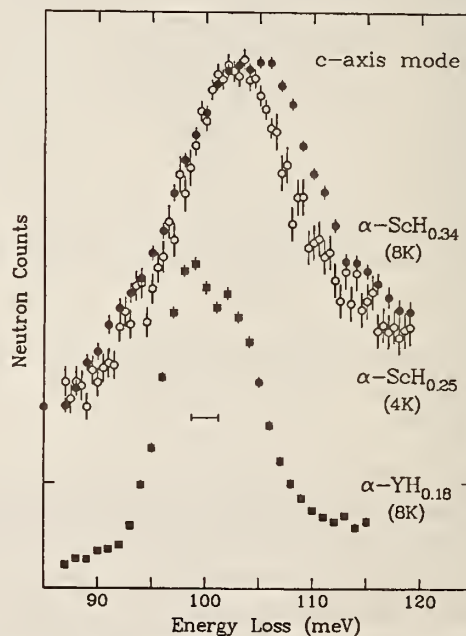


Figure 1. High-resolution IINS spectra of the c-axis mode below 10 K for  $\alpha$ -ScH<sub>0.34</sub> (closed circles),  $\alpha$ -ScH<sub>0.25</sub> (open circles) [1] and  $\alpha$ -YH<sub>0.18</sub> (closed squares) [2]. The instrumental resolution (fwhm) is illustrated by the horizontal bar beneath the spectra.

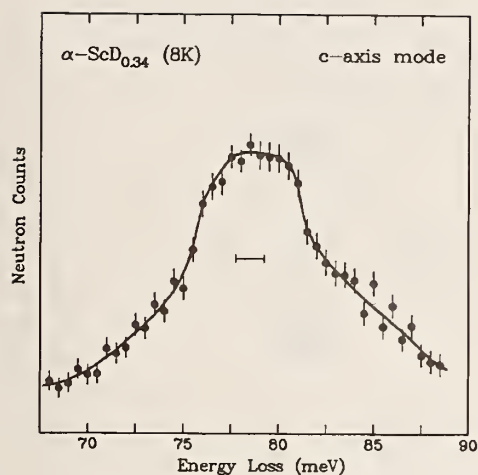


Figure 2. High-resolution IINS spectrum of the c-axis mode at 8 K for  $\alpha$ -ScD<sub>0.34</sub>. The instrumental resolution (fwhm) is illustrated by the horizontal bar beneath the spectrum.

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## OCTAHEDRAL SITE OCCUPATION IN BCC NbV ALLOYS

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Nb<sub>100-x</sub>V<sub>x</sub>H<sub>y</sub> is a random bcc alloy system with a hydrogen sublattice disordered with respect to site energies. Our previous incoherent inelastic neutron scattering (IINS) investigation [1] ascertained both octahedral and tetrahedral site occupation by hydrogen for  $x = 5, 10$ , and 50. On the basis of spectroscopic and statistical arguments, the low temperature vibrational peaks in the Nb-rich Nb-V-H alloys at low H concentration ( $y = 1$ ) were assigned to Nb<sub>4</sub>V<sub>2</sub>-octahedral and NbV<sub>3</sub>-tetrahedral sites.

To more thoroughly investigate the regime of low H concentration and the effects of deuterium substitution, further IINS spectra were measured for Nb<sub>95</sub>V<sub>5</sub>H<sub>y</sub> ( $y = 0.5, 0.8$ ), Nb<sub>95</sub>V<sub>5</sub>D<sub>2.7</sub>, and Nb<sub>95</sub>V<sub>5</sub> with the BT-4 spectrometer using both the Be-filter (low-resolution) and Be-graphite-Be-filter (high-resolution) analyzers. Figure 1 shows the hydrogen vibrational spectra for Nb<sub>95</sub>V<sub>5</sub>H<sub>y</sub> at 4 K, indicating that the vibrational feature at 38 meV becomes more predominant as the H

concentration is decreased. This feature is assigned to the doubly-degenerate hydrogen vibrations in the Nb<sub>4</sub> plane of the Nb<sub>4</sub>V<sub>2</sub> octahedral interstitial site depicted in figure 2. To our knowledge, this is the only known case of octahedral site occupation by hydrogen in a bcc metal (alloy) lattice. Moreover, it is the lowest observed vibrational energy for hydrogen in any metal hydride. Additional IINS measurements of Nb<sub>95</sub>V<sub>5</sub>D<sub>2.7</sub> locate the analogous deuterium vibrational energy at 29 meV, yielding an H to D vibrational energy ratio of 1.31. The higher-energy peaks in the IINS spectra of figure 1 are due to tetrahedral-site occupation as well as an overtone of the 38 meV fundamental vibration. Measurements are under way to determine the energy of the nondegenerate vibration along the V-V axis for H and D in this Nb<sub>4</sub>V<sub>2</sub> octahedral site. For monoclinic  $\beta$ -V<sub>2</sub>H, the analogous octahedral H vibration occurs at 223 meV, much higher than the perpendicular vibrations in the 50-60 meV range [1].

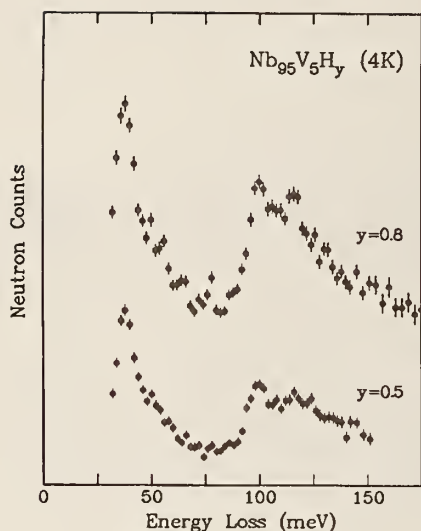


Figure 1. IINS difference spectra of  $\text{Nb}_{95}\text{V}_5\text{H}_y$  -  $\text{Nb}_{95}\text{V}_5$  ( $y = 0.5, 0.8$ ) illustrating the dominant vibrational peak at 38 meV assigned to the doubly-degenerate hydrogen vibrations in the  $\text{Nb}_4\text{V}_2$  site in figure 2.

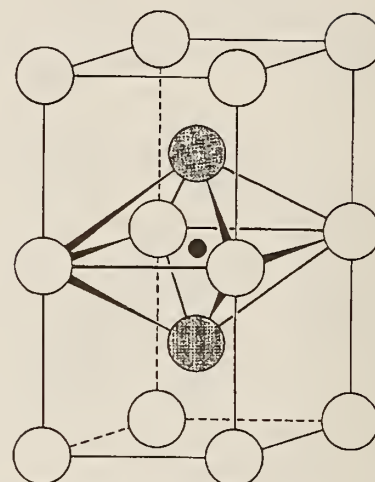


Figure 2. Hydrogen-occupied  $\text{Nb}_4\text{V}_2$  octahedral interstitial site in a random Nb-V bcc alloy (V atoms are shaded.)

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## NEUTRON DIFFRACTION STUDIES OF SOLID $\text{C}_{60}$

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We have made neutron diffraction measurements of the structure of  $\text{C}_{60}$  below and above the order-disorder transition temperature  $T_c = 249$  K [1]. The two samples used in these experiments were prepared by standard techniques, taking precautions to minimize the amount of hydrogenous material in the final product. Their combined weight was approximately 2.4 g. The measurements were performed at the BT-1 spectrometer using 1.545 Å neutrons, with the sample in a vanadium container. The measured diffraction patterns, parts of which are shown (on the same intensity scale) in figures 1 and 2, are similar to previously published x-ray measurements [1],

but because the neutron form factor is independent of scattering angle the high angle scattering pattern is more clearly apparent.

The most remarkable feature in the room temperature diffraction pattern is the diffuse scattering, which peaks at wave vector transfers  $Q$  of  $\sim 3.4$  and  $\sim 5.8$  Å<sup>-1</sup> with a broad shoulder at  $\sim 4.8$  Å<sup>-1</sup>. This scattering, which is also visible in the x-ray measurements [1], is disorder scattering associated with randomly oriented molecules located on a crystal lattice. The complete scattering may be written (per molecule) [2] as

$$S_{\text{dis}}(Q) = \langle F^2(Q) \rangle + \langle F(Q) \rangle^2 [S_C(Q) - 1],$$

where  $F(Q)$  is the molecular form factor,  $S_C(Q)$  represents scattering associated with molecular centres, and  $\langle \dots \rangle$  denotes an average over molecular orientations. Note that as  $Q \rightarrow \infty$ ,  $\langle F^2(Q) \rangle \rightarrow 60$ ,  $S_C(Q) \rightarrow 1$ , and  $\langle F(Q) \rangle^2 \rightarrow 0$ . The calculated profile in figure 1 is simply  $S_{\text{dis}}(Q)$  for a face-centred cubic lattice with  $a_0 = 14.17 \text{ \AA}$  [1] plus a flat background, convoluted into the instrumental resolution and scaled; intra-pentagon and inter-pentagon nearest C-C bond distances were fixed at 1.45 and 1.40  $\text{\AA}$ , respectively. The agreement with experiment, including the shoulder, is remarkably good. This model satisfactorily describes the large  $Q$  pulsed neutron diffraction results of Li et al. [3].

The 14 K pattern (fig. 2) indexes on a simple cubic lattice [1]. Following Sachidanandam and Harris [4] we assume that the space group of the ordered structure is  $\text{Pa}\bar{3}$ . In Rietveld refinements we have found that the "background" under the 14 K diffraction pattern has the same general shape as the diffuse scattering observed at room temperature. We have therefore modelled the scattering as a sum of three terms: (i)  $S_{\text{ord}}(Q)$ , which is the diffraction pattern for ordered  $\text{C}_{60}$  molecules located as described in ref. [4], with  $\Gamma$  (cf. ref [1]) equal to  $24^\circ$ ,  $a_0 = 14.04 \text{ \AA}$  [1], and the temperature factor  $B = 0.3 \text{ \AA}^2$ , (ii)  $S_{\text{dis}}(Q)$  (using the same C-C distances as at 295 K), and (iii) a constant background. These three terms, appropriately scaled and broadened, together give a very good account of the observed scattering, as seen in figure 2. Our calculations suggest that about 30% of the structure is orientationally disordered at 14 K (cf. refs. [1] and [4]).

In order to ascertain the nature of the orientational disorder we have also made quasielastic scattering measurements, described on page 62 in this report.

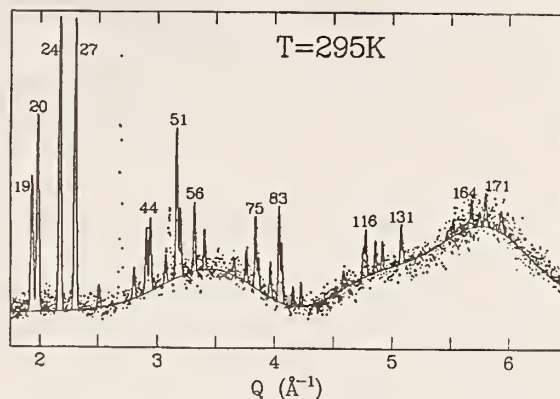


Figure 1. Measured (points) and calculated (line) scattering patterns for  $\text{C}_{60}$  at 295 K. Several peaks are labelled with the quantity  $(h^2+k^2+l^2)$ . Peaks at  $\sim 2.7$  and  $\sim 3.1 \text{ \AA}^{-1}$  are due to aluminum in the beam. The lower line shows  $[\langle F^2 \rangle - \langle F \rangle^2]$ .

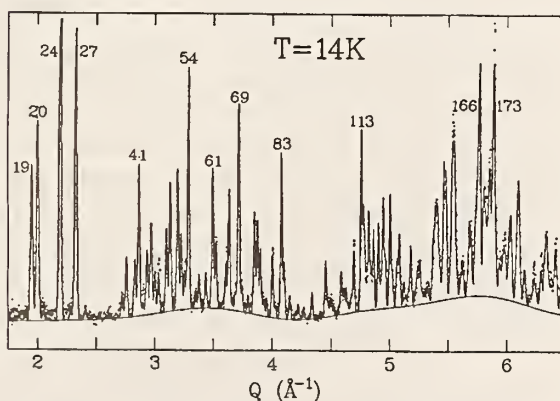


Figure 2. Measured (points) and calculated (line) scattering patterns for  $\text{C}_{60}$  at 14 K. Several peaks are labelled with the quantity  $(h^2+k^2+l^2)$ . The lower line shows  $[\langle F^2 \rangle - \langle F \rangle^2]$ .

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VIBRATIONAL SPECTROSCOPY OF  $C_{60}$  AND GRAPHITIC CARBONS

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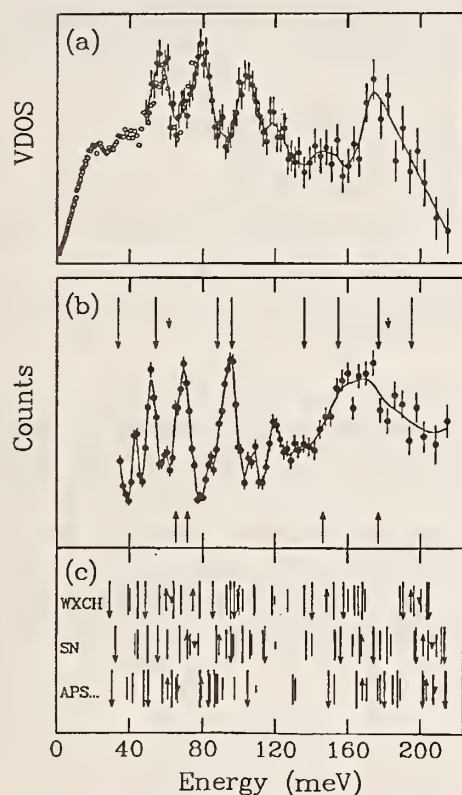
Methods [1] for making bulk quantities of a remarkable new form of elemental carbon,  $C_{60}$  or buckminsterfullerene, have recently been developed, stimulating intensive research on the properties of the  $C_{60}$  solid. The structure of the  $C_{60}$  molecule is a truncated icosahedron, in which the C-C bonds form a pattern exactly like the seams on a soccer ball made up of twenty hexagonal and twelve pentagonal panels. Considering only molecular symmetry, all C atoms are equivalent and are sited on the surface of a perfect sphere. There are many other kinds of interesting carbon solids. Among the latter are so-called glassy carbon, actually a nanocrystalline material, carbon aerogels, which can have densities as low as  $0.04 \text{ g/cm}^3$ , and various crystalline and amorphous carbons made by thin film deposition. We are in the process of making a systematic study of the vibrational densities of states of a wide variety of carbon solids. So far, we have completed neutron measurements of vibrational spectra of pure  $C_{60}$ -fullerite [2], glassy carbon, and graphite. "Glassy" carbon is made by high-temperature decomposition of organic polymers to form a hard, brittle, disordered phase. Our sample has a diffraction pattern resembling graphite but consisting of much broader peaks consistent with crystalline order over a few nanometers. The present results indicate a number of important similarities as well as differences in the vibrational spectra.

Our sample of  $C_{60}$  was prepared at Penn State University, while our glassy carbon sample was manufactured by Sloan, Inc. Most of the data at 14 K were obtained on a triple-axis spectrometer at NIST, using Be or Be/graphite filter analyzers. Low energy data for glassy carbon and for graphite powder were obtained at room temperature on a time-of-flight spectrometer at the Institut Laue-Langevin, Grenoble.

The time-of-flight data for glassy carbon were corrected for multiphonon scattering and converted to a vibrational density of states (VDOS). Although no such conversions or corrections, apart from subtraction of background and container scattering, were applied to the Be-filter data, the latter are expected to give directly the general shape of the VDOS. The two data sets on glassy carbon were scaled to match the peaks between 40 and 80 meV.

Our results are shown in figure 1. Open and closed circles represent data taken with the time-of-flight and Be-filter methods respectively. The spectrum for glassy carbon, shown in figure 1(a), has four major features above 30 meV, at 57, 80, 103, and 177 meV. We also made Be-filter and time-of-flight measurements on pure graphite powder. The result was nearly identical to figure 1(a) for glassy carbon, except that the shoulder in the latter result, which starts at about 18 meV, becomes a sharp cusp at 16 meV, corresponding to the zone boundary interlayer longitudinal mode of graphite. Thus the glassy carbon spectrum is essentially that of graphite, with only a rounding of a low energy Van Hove singularity to mark the presence of disorder. Very broad diffraction peaks, with widths of about  $0.3 \text{ \AA}^{-1}$  ( $3 \text{ nm}^{-1}$ ), were obtained for the glassy carbon sample, indicating that crystalline order only extends over a few nm. Nonetheless, it is more reasonable to regard glassy carbon as a highly disordered crystalline material than as amorphous, since the hexagonal layered structure of graphite is preserved out to several coordination shells.

The  $C_{60}$  results are shown in figure 1(b). Of the 46 distinct frequencies [3] for the 174 internal modes of each molecule, only 4 are infrared-active and 10 are Raman-active; 8 of the 10 Raman modes have been unambiguously



**Figure 1.** (a) Vibrational density of states (VDOS) for glassy carbon, and (b) intramolecular vibrational spectrum for  $C_{60}$ . Lines through points are guides to the eye. Upward (downward) pointing arrows represent observed [4] infrared- (Raman-) active modes. (c) Calculated vibrational frequencies for  $C_{60}$ , according to refs. 5, 6, and 7. In both (b) and (c), the length of a line or arrow is proportional to the degeneracy of the mode.

identified to date [4]. Neutron spectroscopy provides sensitivity to all modes, and the spectrum in ref. 2, most of which is shown here,

is thought to be a complete representation of the intramolecular vibrational modes. There have been several quantum mechanical model calculations of the vibrational modes of the  $C_{60}$  molecule. Results of three calculations [5-7] are shown in figure 1(c). When folded with experimental resolution, the calculations yield spectra qualitatively similar to experiment, but with significant discrepancies. For example, the theories predict a deep minimum near 180-195 meV, whereas none is observed.

The major features of the spectrum in figure 1(b) occur at 53, 69, 95, and 170 meV. The spectrum of  $C_{60}$  thus looks very much like that of a glassy carbon (or graphite) but is red-shifted an average of 8%. The resemblance no doubt arises from the similar three-coordination of atoms in these materials.

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# QUASIELASTIC NEUTRON SCATTERING STUDY OF THE ROTATIONS OF $C_{60}$ IN THE SOLID PHASE

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The existence of an orientational order-disorder transition in the solid phase of  $C_{60}$  has been clearly demonstrated by the neutron diffraction results of Copley et al. [1] (see pg. 58 in this report) and by the x-ray results of Heiney et al. [2]. In order to ascertain whether the orientational disorder above  $T_c$  is static or dynamic, quasielastic scattering measurements have been made using the BT-2 and BT-9 triple axis spectrometers at the NBSR with an energy of 14.8 meV and an elastic energy resolution of 0.48 meV. The rather high incident energy was necessary to reach the first peak in the diffuse scattering. The background was measured by offsetting the analyzer by  $5^\circ$  and the average value was subtracted. The data obtained with the fixed final energy configuration were corrected for second order contamination in the monitor, while those collected with the fixed initial energy configuration were corrected for the resolution volume of the secondary spectrometer.

Spectra obtained below and above  $T_c = 249$  K [2] are shown in figure 1. Closed circles are the experimental data whereas the solid line is a fit to a  $\delta$ -function plus a Lorentzian, convoluted with a Gaussian resolution function. In the ordered state, the scattering is purely elastic within the resolution of the spectrometer, but above  $T_c$  there is clearly a Lorentzian component shown as the dashed line in figure 1. The unmistakable conclusion is that the  $C_{60}$  molecules are rapidly rotating in the high temperature phase. The width of the Lorentzian component indicates that the rotational time scale is 1-10 ps; the exact value depends on details of the rotational motion. This result is consistent with values of 12 ps inferred from NMR measurements at 300 K [3] and 5 ps from

molecular dynamics simulations [4]. Note that the intensity scales are not directly comparable. Furthermore, no blank has yet been measured so that it is not clear whether the  $\delta$ -function component is due to scattering from the can, intrinsic to the  $C_{60}$  molecules, or a combination. These uncertainties will be resolved in future experiments.

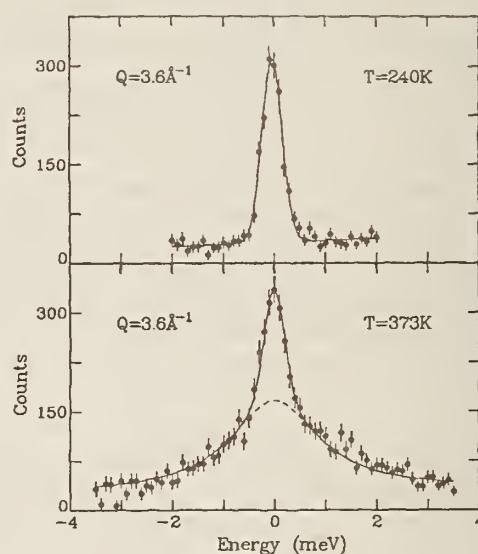
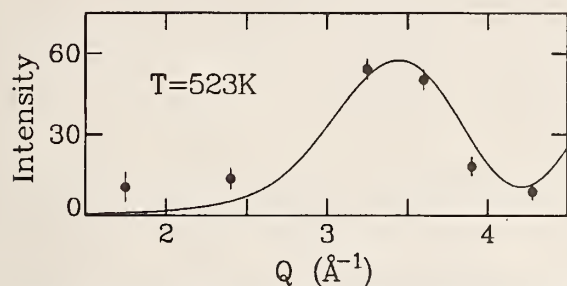


Figure 1. Quasielastic neutron scattering spectra above and below the orientational order-disorder transition.

The points in figure 2 show the integrated intensity of the Lorentzian component as a function of  $Q$  at a temperature well above  $T_c$ . The apparent agreement with the calculated diffuse scattering function,  $\langle F^2 \rangle - \langle F \rangle^2$ , further confirms that the high temperature diffuse scattering is dynamic in origin. Here  $F$  is the molecular form factor and the angle brackets indicate an average over all orientations. On the other hand, the nature of the diffuse scattering at low temperatures is not

as obvious, and experiments to examine this question are in progress.



**Figure 2.** Integrated intensity of the Lorentzian component as a function of  $Q$  (solid points), and the quantity  $[\langle F^2 \rangle - \langle F \rangle^2]$  (solid line).

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## NEUTRON SCATTERING STUDIES OF Cs-AMMONIA INTERCALATED GRAPHITE

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Neutron scattering is an ideal tool for the study of the dynamics of alkali-ammonia graphite intercalation compounds. Previous work [1] on the K-ND<sub>3</sub> system has revealed a hybridization of the [OOL] longitudinal acoustic phonons with a mode of the "liquid" intercalate layer at an energy of about 7 meV. To date three different models for this intercalate mode have been proposed. The first model is that the excitation is a libration of the ammonia molecule about its C<sub>3</sub> symmetry axis which lies in the basal plane [2]. This model seems doubtful in light of results which show that the activation energy in the low temperature solid intercalate phase in both K-ammonia [3] and Cs-ammonia [4] intercalated graphite is about 6 meV. Thus at room temperature (about 25 meV), one would expect the ammonia molecule to be "freely" rotating and would therefore not hybridize with the phonons in the manner observed. In the second model, the mode is a libration of the ammonia in the potential created by the screened charge-dipole interaction responsible for the formation of the K-ammonia complexes observed

by Solin and co-workers [2]. In the third model the K ion vibrates along the c-axis due to the relatively small size of the K ion compared to the hydrogen plane of the ammonia molecule [5]. Thus the second and third possibilities involve the alkali ion either directly or indirectly so that changing the alkali ion should alter the mode which couples to the phonons. We have therefore undertaken a neutron scattering study of CsC<sub>24</sub>(ND<sub>3</sub>)<sub>3.7</sub> devised as a test of these models.

Figure 1 shows in-plane elastic scans of the liquid intercalate for KC<sub>24</sub>(ND<sub>3</sub>)<sub>4.3</sub> (solid line) and CsC<sub>24</sub>(ND<sub>3</sub>)<sub>3.7</sub> (closed circles). Note that the peak at about 20 nm<sup>-1</sup> is narrower for the Cs compound than for the K one. This indicates that the ammonia-ammonia correlations, which dominate the scattering, are somewhat longer range in Cs-ammonia intercalated graphite than for its K counterpart. In addition, the peak at about 8.5 nm<sup>-1</sup> in the K-compound is replaced for the Cs case by substantial small angle scattering. This shows that while some sort of clusters have formed in the Cs compound, they

are different than the fourfold complexes found in the K analog. Thus the potential due to the screened charge-dipole interaction responsible for the complex formation has, to at least some extent, been modified.

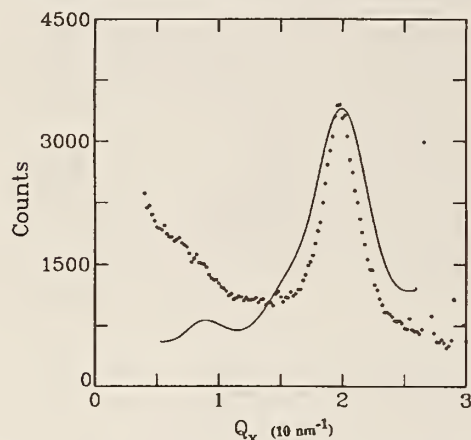


Figure 1. In-plane elastic scan of the liquid intercalate structure. The closed circles are the data obtained for  $\text{CsC}_{24}(\text{ND}_3)_{3.7}$  while the solid line is the same scan for  $\text{KC}_{24}(\text{ND}_3)_{4.3}$  taken from reference [2].

Figure 2 shows the [OOL] longitudinal acoustic phonon branch for both the K-ammonia (open circles) and Cs-ammonia intercalated graphite (closed circles). Here the solid (Cs) and dashed lines (K) represent fits of the dispersion to a 1-d Born-von Karmen model coupled to an Einstein oscillator of energy  $\alpha$ . The fit parameters reflect three features readily observed in the data. First, the observation that the  $\text{CsC}_{24}(\text{ND}_3)_{3.7}$  is somewhat stiffer than  $\text{KC}_{24}(\text{ND}_3)_{4.3}$  is exhibited in the values of the force constant  $\phi$  which were found to be 2.31 N/m for the Cs compound compared to 2.02 N/m for the K one. The reason for this change in the force constant may be the reduced charge back-transfer from the graphite pi orbitals to the intercalate layer of the Cs-ammonia system. The second fit parameter shows that  $\alpha$  is only slightly larger (7.1 meV compared to 6.8 meV) for the Cs-ammonia system. This indicates that the mode is not simply a motion of the alkali ion and suggests that the alkali-ammonia interaction has not been appreciably altered even though the intercalate structure seems to be quite different or alternatively that this interaction is not the origin of the librational potential of the molecule. Finally, the splitting of the acoustic

branch is much larger in  $\text{CsC}_{24}(\text{ND}_3)_{3.7}$  than in  $\text{KC}_{24}(\text{ND}_3)_{4.3}$ .

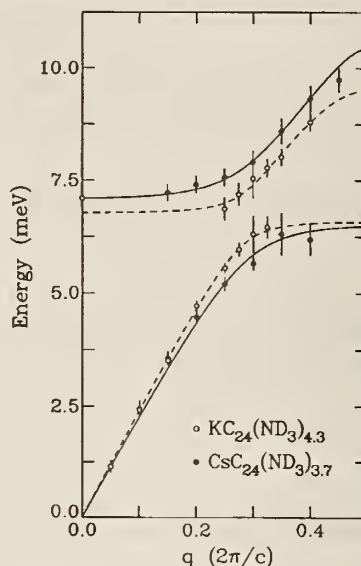


Figure 2. [OOL] longitudinal acoustic phonon dispersion obtained for  $\text{CsC}_{24}(\text{ND}_3)_{3.7}$  (solid circles) and for  $\text{KC}_{24}(\text{ND}_3)_{4.3}$  (open circles) taken from reference [1]. The solid and dashed lines represent fits to the data.

In summary, the [OOL] longitudinal acoustic phonons in  $\text{CsC}_{24}(\text{ND}_3)_{3.7}$  and a hybridization of these phonons with a librational mode of the ammonia have been observed. Through comparison of these results with those in the analogous K compound, we have been able to show that this mode does not involve an excitation of the alkali ion. In addition, we take the large change in the liquid diffraction pattern of the intercalate layer as an indication that the alkali-ammonia interaction is not the principal source of the librational potential. Thus this mode is almost certainly a libration in a potential created by either graphite-ammonia or ammonia-ammonia interactions or both.

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## LATTICE DYNAMICS OF HEXAGONAL BORON NITRIDE

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Graphite is the prototypical layered solid, consisting of planar hexagonal sheets of three-coordinated carbon atoms linked with very strong covalent bonds, and much weaker van der Waals interactions between layers. A close analogue to graphite is hexagonal boron nitride (h-BN), formed from the neighboring elements to carbon in the periodic table. In contrast to graphite, which is a semimetal, h-BN is an insulator with a 5 eV bandgap. It is an extensively used ceramic in high-temperature applications. The structure of h-BN comprises planar layers in which each atom type, B or N, is three-coordinated with atoms of the other type. The interlayer structure forms strings of alternating atoms BNBNNB... spaced 3.35 Å along the c-axis. This differs to some extent from graphite, in which the stacking places half the atoms in such strings, with the others facing voids at hexagon centers instead of atoms in adjacent layers. The chief microscopic difference between graphite and h-BN is the partially ionic character of the latter.

Single crystals of h-BN of the size required for neutron inelastic scattering are unavailable. However, a c-axis-aligned form, referred to as highly-oriented pyrolytic boron nitride, or HOPBN, in analogy to the HOPG form of graphite, has recently been successfully prepared at the Parma, Ohio laboratories of Union Carbide. The best quality samples of HOPBN have c-axis mosaic spreads of  $\sim 2^\circ$ . Using a composite sample comprising three such pieces of HOPBN, we have been able to measure phonon dispersion curves for (i) [001]L rigid-layer modes with wave vectors parallel to the c-axis, and (ii) layer-bending modes propagating parallel to the layers.

We find (fig. 1) that the [001]L modes have significantly lower frequencies than the analogous modes of graphite. This is somewhat surprising, since the ionic character and interlayer stacking would both have led one to expect

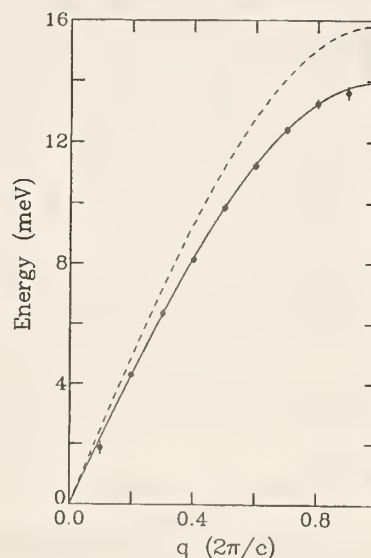


Figure 1. [001]L phonon dispersion of hexagonal boron nitride (points and solid line), and of graphite (dashed line, from ref. 1).

increased interlayer interactions. The dispersion for layer-bending modes [2] (fig. 2) is characteristic of a layered compound, with a pronounced upward curvature to the acoustic branch. Higher-resolution measurements on this branch are needed to extract elastic constant  $C_{44}$ , which characterizes the resistance of the layers to a rigid-layer transverse shearing motion. Also planned are measurements of out-of-plane vibrational modes in which nearest-neighbor B and N atoms within the same layer are displaced in opposite directions along the c-axis. Although it is important to include such modes to obtain a realistic picture of the lattice dynamics of HOPG, for that material they are difficult to measure, since their structure factor goes to zero for  $\vec{Q}$  parallel to  $\vec{c}$ . The different scattering lengths of B and N should give them an appreciable structure factor for the case of HOPBN. Thus we will be able to characterize both intralayer and interlayer interactions in a straightforward manner.

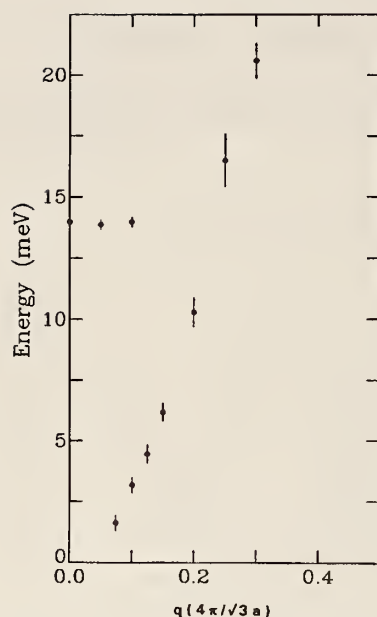


Figure 2. Phonon dispersion for layer bending modes of HOPBN.

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## LOW-ENERGY NETWORK DYNAMICS OF SILICA AEROGELS

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Silica aerogels are random-network, low-density microstructures whose dynamics are currently not well understood. These materials are chemically similar to amorphous silica ( $\alpha$ -SiO<sub>2</sub>) but their novel microstructure gives rise to very different low energy dynamics. Specifically, the density of network excitations below 1 meV can be as much as two orders of magnitude larger than in  $\alpha$ -SiO<sub>2</sub>.

In the present study we investigate a series of porous silica aerogels having qualitatively different microstructures and connectivities in order to characterize their relative low-energy dynamic responses. Neutron spin-echo (NSE) and time-of-flight (TOF) spectrometers were used to measure an effective density of states,  $g(E)$ , covering four decades in energy transfer  $E$ . TOF diffraction measurements were also carried out to characterize the atomic arrange-

ments of this same aerogel series for wave vectors up to 40 Å<sup>-1</sup>.

Two primary types of microstructures exist in our aerogel series. One is a polymeric (polymer-like) network, while the other is a colloidal (particle-like) network [1]. The difference, as determined using small-angle neutron scattering (SANS) techniques, is shown in figure 1. The polymeric aerogel has a Porod slope greater than -3 thus indicating that the corresponding network is self-similar (fractal) on a length scale between ~ 10 to 100 Å. In contrast, the colloidal microstructure shows a Porod slope of -4, indicative of a nonfractal, smooth particle network.

The low energy dynamics, as measured by NSE, of these contrasting microstructures show markedly different behavior. For example, the colloidal aerogel has a peak in  $g(E)$  for network

excitations in the 10 - 20  $\mu\text{eV}$  range (see fig. 2). Polymeric aerogels show no such peak, but only a continuum of network excitations which can be interpreted in terms of the fracton model [2]. The polymeric aerogel is power-law from 10 - 100  $\mu\text{eV}$  with a slope of  $\sim 0.5$ .

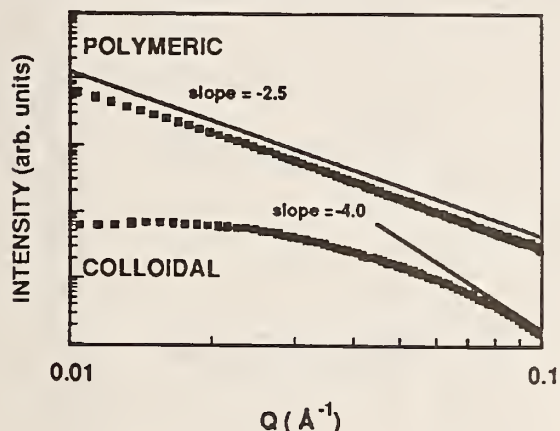


Figure 1. SANS curves for the polymeric vs. colloidal aerogel microstructure. The slope greater than - 3 indicates the polymeric aerogel has a self-similar network.

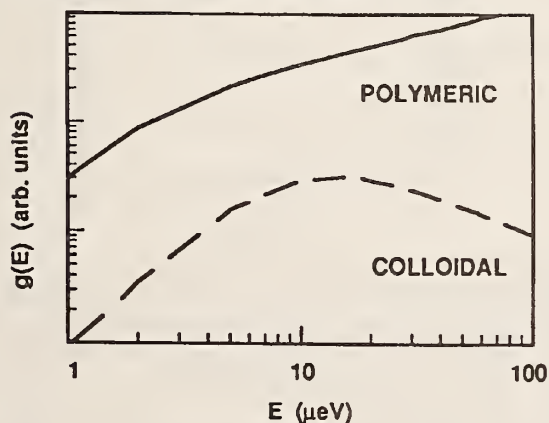


Figure 2. Effective density of states,  $g(E)$ , for the polymeric vs. colloidal microstructure as calculated in the NSE (IN11) energy window. Note the  $g(E)$  are not actual data but rather fits to the measured intermediate scattering function  $S(Q,t)$  (see ref. [1]).

The intermediate energy dynamics, as measured by TOF, of the colloidal vs. polymeric microstructure also show power-law behaviors that are markedly different from one another. In figure 3 are the TOF energy transfer spectra of the two contrasting microstructures. The polymeric aerogel shows slightly less than a decade of power-law behavior in  $g(E)$ , which may also be interpreted within the fracton

model. However, the slope here,  $0.1 < E < .75 \text{ meV}$ , is  $\sim 0.75$ . The origin of the change in slope from 0.5 to 0.75 is not understood. The polymeric aerogel shows evidence of an additional crossover at  $E \sim 0.75 \text{ meV}$ . The origin of this crossover lies in changes in the solution precursor chemistry. The colloidal aerogel shows a more extensive power-law regime (slightly more than a decade). The linear behavior in  $g(E)$  for this material, however, cannot be interpreted within the fracton model since the microstructure, from SANS, shows no evidence of a fractal network.

The SANS data were obtained at the Oak Ridge and Los Alamos National Laboratories. All inelastic measurements were made at the Institut Laue-Langevin in Grenoble, France, using a combination of the IN6 (TOF) and IN11 (NSE) spectrometers.

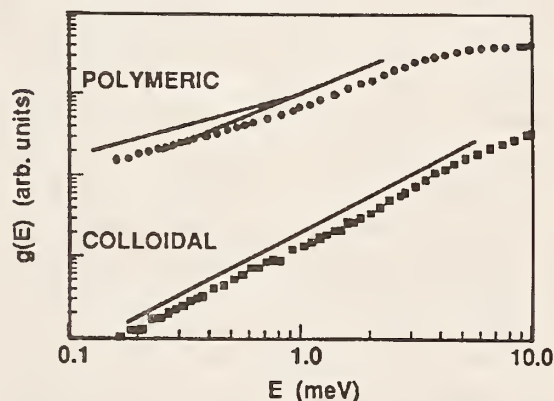


Figure 3. Effective density of states,  $g(E)$ , for the polymeric vs. colloidal microstructure as seen in the TOF energy window. Data were taken on IN6 at 300 K.

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## STRUCTURE AND DYNAMICS OF POTASSIUM SILICATE GLASS

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Alkali silicate glasses, produced by the addition of  $\text{Na}_2\text{O}$ ,  $\text{Li}_2\text{O}$ , and  $\text{K}_2\text{O}$  to  $\text{SiO}_2$ , have structures and dynamical properties substantially different from the parent  $\text{SiO}_2$  glass. For example, the addition of the above oxides changes the viscosity, softening temperature, and thermal expansion coefficient of the a- $\text{SiO}_2$  network [1]. The effect of these modifiers is to introduce excess nonbridging oxygen atoms, i.e., oxygens which do not link adjacent  $\text{SiO}_2$  tetrahedra. The  $\text{K}^+$  cations, moreover, are not covalently bonded to the network and can, under certain conditions, migrate around these nonbridging oxygen atoms. The relationship between the structure of the disrupted networks and the vibrational dynamics is not fully understood.

We have begun a systematic study on a series of silica based glasses (potassium silicates) in order to expand current understanding of the dynamics of these important amorphous materials. We have chosen the series  $(\text{SiO}_2)_{1-x}(\text{K}_2\text{O})_x$  for several reasons. First, the concentration of  $\text{K}_2\text{O}$  cations can be varied over a wide range,  $0.1 < x < 0.55$ , so that trends can be followed into a regime where large changes from the a- $\text{SiO}_2$  structure are present. Some of our early results from the BT-4 spectrometer (fig. 1), indicate significant changes in the dynamic response for the energy transfer range,  $60 < E < 160$  meV. For example, the entire spectrum of the 50%  $\text{K}_2\text{O}$  appears down shifted by  $\sim 20$  meV from undoped a- $\text{SiO}_2$ .

We believe that the substitution of the potassium atoms is random, in contrast to earlier findings for lithium and sodium silicates [2]. We have taken diffraction data, some of which is shown in figure 2, in order to explore this question of random vs. nonrandom substitution. The diffraction data were also taken on the BT-4 spectrometer and they reveal a radical modification of the unadulterated a- $\text{SiO}_2$  structure. Unfortunately, the short range in  $Q$  prohibits us

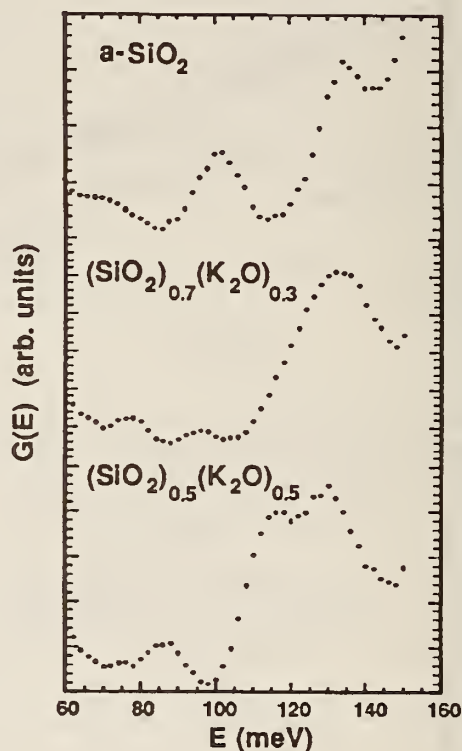


Figure 1. The effective density of states,  $G(E)$ , for amorphous silica and the given potassium silicates. The data were taken at 50 K on the BT-4, triple axis spectrometer, in the beryllium filter mode.

from accurately Fourier transforming the data into the corresponding radial distribution function. We have recently obtained data on a pulsed source (HIPD at Los Alamos), hence a much broader range in  $Q$ , so that the question of correlations after substitution can be more accurately explored.

If the substitution of the potassium atoms into the silica network is random, we expect the disruption of the network by the potassium to lead to dynamics somewhat different than the dynamics of correlated substitutions. Existing models are currently being applied to our inelastic data. More data, however, is desirable at higher energy transfers,  $E > 150$  meV.

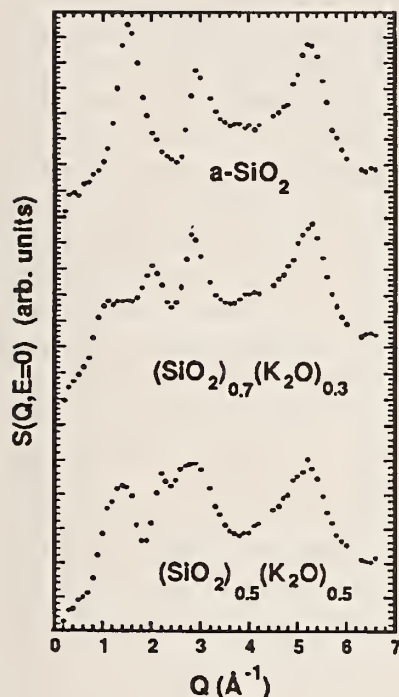


Figure 2. The elastic structure factor,  $S(Q, E = 0)$ , for  $a\text{-SiO}_2$  and the potassium silicates shown in figure 1. The data were taken at 300 K on the BT-4 triple axis spectrometer.

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## STRUCTURE OF NITROGEN IN POROUS VYCOR GLASS

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and  
S. K. Satija

The properties of liquids and solids confined in small pores has generated significant interest recently [1]. A number of interesting effects have been observed which are common to many systems. Among the most interesting [2] is the observation of supercooling, a depression of the temperature of phase transitions below their bulk value, and hysteresis of the phase transitions between cooling and warming. These effects have been observed for both liquid-solid and solid-solid phase transitions. The degree of supercooling is inversely related to the pore size and has been interpreted using a geometrical supercooling model. The collective properties of confined liquids and solids are also significantly different from those of the bulk system.

Despite the great amount of experimental work on these systems there is little direct information on the microscopic structure of the liquid or solid in the pores, such as obtained

from X-ray or neutron scattering measurements. In the liquid, the local environment and bonding of a particle is directly reflected in the short range structure. In the solid, the spatial arrangement of the atoms or molecules composing the solid can be obtained. Thus structural studies address such basic questions as whether the solid phase in the porous media is crystalline or amorphous and whether the structure is the same as the bulk structure.

We have studied the structure and phase transitions of nitrogen adsorbed in porous vycor glass. Vycor glass is formed by spinodal decomposition of a boro-silicate glass at high temperature followed by leaching out of the boron rich phase. The porosity of the resulting glass is  $\sim 0.31$  and the network of pores is highly interconnected. In addition, the pores have a fairly narrow size distribution with a nominal pore diameter of 70 Å. Nitrogen

provides an interesting system for study since it has both a liquid-solid and solid-solid phase transitions. In the bulk, nitrogen solidifies into a hcp structure at 63 K and undergoes a first order phase transition to a fcc structure with rotational ordering at 35 K.

The measurements were carried out on the BT-6 spectrometer with a fixed incident energy of 14.8 meV. Data was collected for momentum transfers between 0.5 and 4.3  $\text{\AA}^{-1}$  at increments of 0.01  $\text{\AA}^{-1}$ . The vycor sample, produced by Corning Glass Co., was cleaned by slowly heating the glass to 600 C under vacuum and occasionally flushing with oxygen. The sample was transferred to an aluminum sample cell in a glove box to prevent contamination. The pores were filled with nitrogen at 70 K, in the liquid phase, to  $\sim 90\%$  of their capacity. Slightly underfilling the pores prevented the formation of bulk regions in the sample.

Figure 1 shows the scattering from nitrogen in vycor, with the background from the Al cell and the vycor glass subtracted, at three different temperatures. The scattering at 70 K, which corresponds to the bulk liquid phase, exhibits the characteristic scattering for a liquid. Comparisons to the bulk liquid structure are currently under way.

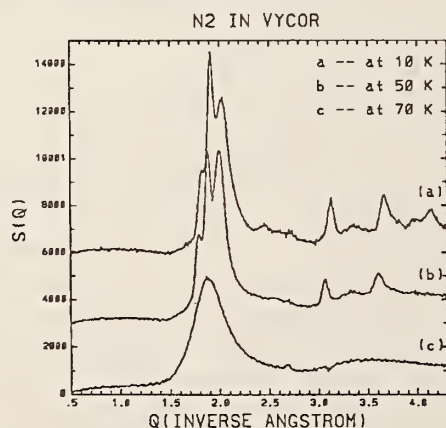


Figure 1. The scattering from nitrogen in vycor at temperatures of 10, 50, and 70 K. These correspond to the bulk fcc, hcp, and liquid phases. The background from the aluminum cell and the vycor glass has been subtracted. The zero of the scattering has been shifted to show the scattering more clearly.

A sharp transition, marked by the appearance of diffraction peaks, occurs at 59 K, well below the bulk liquid-solid transition

temperature. This supercooling of the liquid solid transition has been observed for many other systems [2]. The diffraction peaks are a clear and unambiguous indication that long range positional correlations are present and that solidification has occurred. The location of the diffraction peaks agree well with those for the bulk beta phase of nitrogen, indicating that this phase has the same symmetry as the bulk solid. The intensities of the peaks are different, possibly due to different orientational correlations of the nitrogen in the vycor.

The hcp to fcc transition in the bulk, which occurs at 35 K, is not observed for the nitrogen in vycor down to temperatures of 4.5 K. The location of the peaks is always consistent with a hcp, and not fcc, structure. Thus, the solid-solid transition is suppressed in the presence of Vycor glass. We do, however, observe a fairly rapid change in the relative intensities of the diffraction peaks below 35 K. We are currently exploring the nature of these changes. One possibility is that orientational ordering occurs, but without the lattice change that is observed in the bulk systems. Whether these changes represent a phase transition or simply a continuous change in the orientational order is not yet clear.

The observed diffraction peaks are significantly broader than the instrumental resolution. This broadening can be due to several factors such as the finite crystallite size, strains, defects, etc. The contributions of these various effects depends on the detailed nature of the crystallites, the strains, etc. However, a rough estimate gives an average size [3] on the order of 400  $\text{\AA}$ , much larger than the average pore diameter. This implies that crystalline regions must extend a substantial length down the pores or even between pores.

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## SELF-DIFFUSION IN A MICROPOROUS MEDIUM

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There has been a great deal of progress in recent years in the understanding of flow of liquids in porous media and its relation to the microstructures of the materials, due to the importance of the subject in both scientific understanding and technological applications. The permeability for viscous flow is given by  $\kappa = b\phi a^2/\tau$  where  $b$  is a dimensionless factor whose value depends on the shape of the cross-section,  $\phi$  is the porosity,  $a$  is an average pore radius and  $\tau$  is the tortuosity. While  $\phi$  and  $a$  can be determined from measurements of the isotherms, the tortuosity  $\tau$  must be determined from transport measurements. The most direct way of determining  $\tau$  is from the relationship  $\tau = D/D_p$  where  $D$  and  $D_p$  are the diffusion coefficients of the liquid in the bulk state and in the porous medium respectively.

In this work, we use small angle neutron scattering (SANS) to determine the self-diffusion coefficient  $D_p$  of hexane and decane in Vycor. Vycor is a model microporous system with a porosity  $\phi = 0.3$  and an average pore radius of  $a = 30$  Å. In the range of the momentum transfer  $Q$  that is accessible with SANS, the microstructure of Vycor is shown in figure 1 to have the characteristic peak-like structure factor whose amplitude is proportional to the contrast between the solid material ( $\text{SiO}_2$ ) and the material in the pores (either air, vacuum, or fluid) squared,  $I \sim (p_s - p_p)^2$  where  $p_s$ , and  $p_p$  are the neutron scattering length densities of the solid and of the material in the pores respectively.

The Vycor sample was first imbibed with a contrast matching (i.e.,  $p_p = p_s$ ) mixture of  $\text{C}_6\text{H}_{14}$  and  $\text{C}_6\text{D}_{14}$ . The normal hexane ( $\text{C}_6\text{H}_{14}$ ) and the deuterated hexane ( $\text{C}_6\text{D}_{14}$ ) have the same diffusion coefficient but very different neutron scattering length densities, which makes the contrast matching possible with the liquids of the same diffusion coefficient. The self-diffusion

coefficient  $D_p$  was then determined by observing the rise in the SANS intensity  $I$  as a function of time, as the matching fluid in the sample was exchanged through diffusion of  $\text{C}_6\text{H}_{14}$  whose  $p_p \neq p_s$ , from a reservoir in contact with the sample. In figure 1, we plot the SANS intensity  $I(Q)$  as a function of the momentum transfer  $Q$  at three different times. The amplitude of the  $I(Q)$  as a function of time  $t$  is then fitted with a theoretical function calculated for the particular geometry used in the experiment, with the diffusion coefficient  $D_p$  as the fitting parameter. The fitting is shown in figure 2 for the case of another paraffin  $\text{C}_{10}\text{H}_{22}$  (decane). The values of  $D_p$  determined at  $23^\circ\text{C}$  were  $9.9 \times 10^{-6}$  and  $3.2 \times 10^{-6}$   $\text{cm}^2/\text{sec}$  for  $\text{C}_6\text{H}_{14}$  and  $\text{C}_{10}\text{H}_{22}$ , respectively. The tortuosity thus determined is  $\tau = 4.0 \pm 0.1$  for both hexane and decane, independent of the carbon number. We believe that indicates that the size of the alkane molecules is still small enough that the surface-molecule interaction is not significant in these cases.

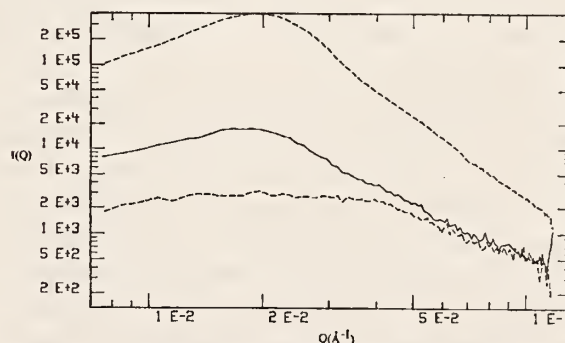
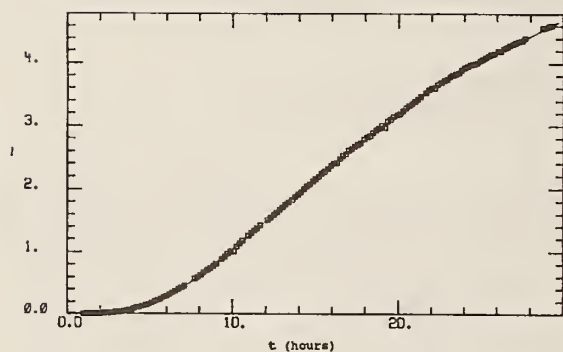


Figure 1. The characteristic structure factor of Vycor is shown as the neutron scattering intensity  $I(Q)$  as a function of the momentum transfer  $Q$ . The three curves were taken at three different times during the diffusion of the non-matching liquid into the Vycor sample. The lowest curve was taken at  $t = 0$ , and as more nonmatching liquid diffuses in, the intensity increases with the shape unchanged.



**Figure 2.** A fit (solid line) to the SANS intensity data (squares) as a function of time of the diffusion process. The experiment lasts for more than a day. The self-diffusion coefficient of decane obtained from the fitting is  $3.2 \times 10^{-6} \text{ cm}^2/\text{sec}$ .

## SUSPENSION STRUCTURE UNDER SHEAR FLOW: SANS STUDY OF THE ORIGIN OF SUPERANOMALOUS FLOW

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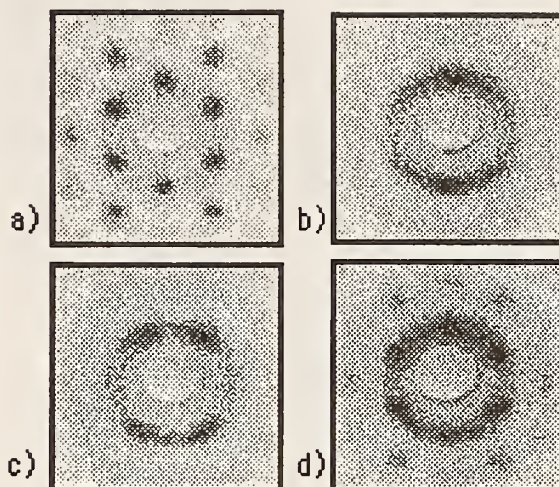
A variety of colloidal suspensions consisting of strongly interacting particles exhibit an abrupt drop in steady state viscosity under certain conditions of shear flow. This behavior, in which an increase in shear rate results in a decrease in shear stress, is referred to as superanomalous flow, or discontinuous shear thinning, and has been the focus of recent SANS measurements using the new 30 m NIST/Exxon/U. of MN SANS instrument. The measurements were made on a suspension of charged 229 nm diam polystyrene spheres (at a volume fraction of 53%) that filled the 0.5 mm gap between the stationary and rotating coaxial cylinders of a quartz shear cell. When properly prepared such suspensions can form highly ordered structures over macroscopic dimensions and serve as model systems for relating mechanical response and suspension microstructure.

Figure 1 shows four representative SANS patterns that were recorded with the incident neutron beam perpendicular to the cylindrical walls of the shear cell at shear rates spanning the region of superanomalous flow. The patterns are gray scale representations of the scattered neutron intensity as recorded on the SANS instrument's 2-d detector. The pattern in figure

1a) was measured with the suspension at rest after shearing at a low rate for several minutes to induce ordering. The characteristic sixfold spot pattern seen in figure 1a) has been observed [1] in a variety of ordered latex suspensions and results from close packed hexagonal layers of particles oriented parallel to the walls of the cell with their close-packed direction parallel to the flow direction. At finite shear rates, below the region of anomalous flow, the SANS pattern evolves to one of nearly uniform concentric rings, figure 1b), which are too sharply defined for a liquid-like structure and indicate, therefore, that the suspension has broken up into nearly randomly oriented polycrystals. As the shear rate is increased into the superanomalous region, discrete diffraction spots start to reappear in the SANS data, figure 1c), indicating a return of longer range order which is restored gradually as the shear rate is further increased. At a shear rate of  $35 \text{ sec}^{-1}$ , a well-defined sixfold spot pattern is observed once again, figure 1d), that remains sharp to shear rates in the vicinity of  $2000 \text{ sec}^{-1}$  where the sample shear melts, loses long range order and becomes dilatant. From these data, together with data taken with the beam shifted off the axis of the shear cell (to

probe the structure along the direction of the velocity gradient), it can be inferred that at low shear rates the suspension has long range ordered close-packed layers that have a random registered stacking in the velocity gradient direction. When long range order is reestablished above the region of anomalous flow, extended oriented layers of close-packed particles form with no correlation in position perpendicular to the layers.

These measurements demonstrate that anomalous flow in this system is associated with a nonequilibrium structural phase transition between two distinct states with long range order. Further experiments are planned on related systems in order to explore the generality of this result.



**Figure 1.** Small angle neutron scattering patterns from an aqueous suspension of 239 nm polystyrene latex spheres measured on the 30 m NIST/Exxon/U. of MN SANS instrument. The patterns correspond to shear rates: a)  $0 \text{ sec}^{-1}$ , b)  $0.08 \text{ sec}^{-1}$ , c)  $0.3 \text{ sec}^{-1}$ , and d)  $35 \text{ sec}^{-1}$ .

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## THE VIBRATIONAL SPECTROSCOPY OF AMMONIUM IONS IN TITANYL PHOSPHATES

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and

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The potassium titanyl phosphate (KTiOPO<sub>4</sub>: KTP) family of phases are currently the subject of great interest due to their technologically important nonlinear and electro-optical properties [1]. In KTP, it is possible to effectively modify the SHG (second harmonic generation) characteristics by replacement of the potassium ions by ion-exchange with other cations, such as NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, Rb<sup>+</sup>. While the ammonium (NH<sub>4</sub>TiOPO<sub>4</sub>: NTP) derivatives, for example, have a similar SHG response to the prototype material, other cations such as Na<sup>+</sup>, can drastically reduce the nonlinear properties. The object of the present study was to examine the vibrational spectroscopy and dynamics of the ammonium derivatives of KTP by inelastic neutron

scattering (INS) and relate the results to the structure and SHG-response of the materials [2].

The KTP structure is characterized by TiO<sub>6</sub> chains crosslinked by phosphate bridges forming a framework with 1-d channels, in which the K<sup>+</sup> cations are located [1]. The Ti-O bonds of the O-Ti-O chains may be regarded as alternate 'single' and 'double', and the resulting polarization difference is believed to be a crucial feature in determining SHG-response. In NTP, neutron diffraction [2], has found two crystallographically distinct NH<sub>4</sub><sup>+</sup> ion sites. Both types of NH<sub>4</sub><sup>+</sup> ions form hydrogen bonds to framework oxygens via two of their four protons. When NTP is partially deammoniated to (NH<sub>4</sub>)<sub>0.5</sub>H<sub>0.5</sub>TP (NHTP), loss of NH<sub>4</sub><sup>+</sup> is

site selective. However, a substantial structural rearrangement takes place. In particular, the long-short Ti-O bond alternation in the chains is lost and the remaining  $\text{NH}_4^+$  shows a different coordination to the oxygens. The SHG response of NHTP is much reduced compared to NTP.

INS spectra were measured for a series of titanyl phosphates including NTP,  $\text{K}_{.61}(\text{NH}_4)_{.39}\text{TP}$  (KNTP),  $\text{K}_{.8}(\text{NH}_4)_{.2}\text{TP}$ , NHTP, and KTP using the BT4 spectrometer with either a beryllium ( $645\text{--}1800\text{ cm}^{-1}$ ) or Be-graphite-Be ( $100\text{--}1130\text{ cm}^{-1}$ ) low-energy-band-pass filter placed before the detector. All spectra were obtained with the samples at 80 K, unless otherwise specified and were corrected for fast neutron background contributions. A single vibrational energy spectrum was obtained by scaling the different energy ranges according to their overlapping regions.

In the high energy INS spectrum of  $\text{K}_{.61}(\text{NH}_4)_{.39}\text{TP}$  the characteristic symmetric and antisymmetric bending modes of the  $\text{NH}_4^+$  ion were observed at  $1440$  and  $1670\text{ cm}^{-1}$  respectively, in agreement with those found for other ammonium-containing materials [3]. An intense band peaked at ca.  $339\text{ cm}^{-1}$  in the low energy spectra of KNTP and NTP (figures 1) is due to the torsional mode of the  $\text{NH}_4^+$  ions. This peak energy compares well with those found for other ammonium salts, e.g.  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  [4] and suggests a comparable reorientational barrier in the range  $10\text{--}20\text{ kJ mol}^{-1}$ . Spectra recorded at 298 K for NTP (and NHTP) show the expected damping of this mode with temperature, suggestive of rapid  $\text{NH}_4^+$  ion reorientations. The shape of the torsional-mode peak is observed to be broad with evidence for a shoulder on the low energy side. This shoulder, together with weak features on the high energy side are possibly due to enhanced scattering intensity from lattice modes which derive their increased intensity from coupling to the  $\text{NH}_4^+$  ions. Indeed, the INS spectrum of KTP displays features due to lattice vibrations in this energy range. The most significant contributions to the observed broadness of the torsional peak may arise from either an asymmetric torsional potential or from the presence of different structural environments for the  $\text{NH}_4^+$  ions.

The sharp peak observed in NTP and KNTP at ca.  $155\text{ cm}^{-1}$ , which broadens on

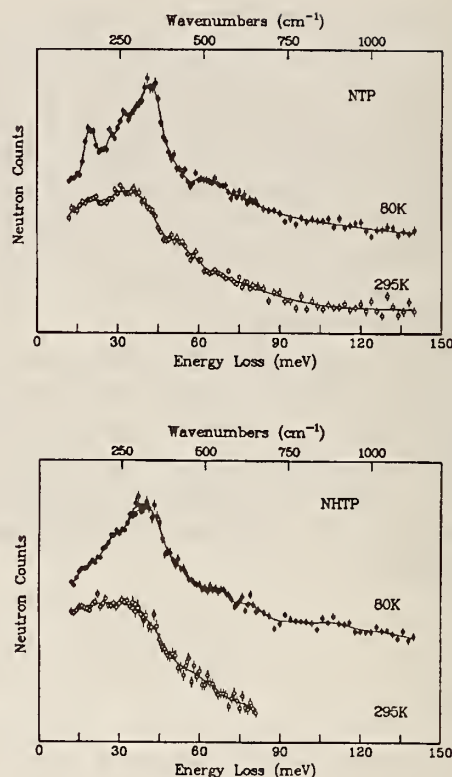


Figure 1. INS spectra of NTP and NHTP at 295 K (open circles) and 80 K (closed circles) collected using the Be-graphite-Be filter. The data have been corrected for fast neutron background contributions. The solid line represents a guide to the eye.

increasing the temperature, is assigned to an optical translatory mode of the  $\text{NH}_4^+$  ions in the lattice. Similar modes have been observed in the ammonium halide salts [4]. This mode is noticeably absent in the INS spectra of NHTP.

The INS spectra of NHTP (figure 1) show different characteristics compared to those observed for either NTP or KNTP. Although the torsional-mode peak of the  $\text{NH}_4^+$  ions is observed at ca.  $323\text{ cm}^{-1}$ , an energy very similar to that found for NTP, the peak is considerably broadened and a separate translatory-mode peak is not observed. These observations all suggest that the  $\text{NH}_4^+$  ions in NHTP experience a different environment from those in either NTP or KNTP. The broadening of the torsional mode and the disappearance of the optical translatory mode on deammoniation indicate an  $\text{NH}_4^+$  ion that is more 'floppy', i.e. less tightly bound. The vibrational energy of the torsional mode, however, suggests that the average rotational barrier is not significantly altered by

deammoniation. These observations are supported by crystallographic data [2]. For, although only  $\text{NH}_4^+$  ions at one crystallographic site are depleted during deammoniation, the  $\text{NH}_4^+$  ions remaining are crystallographically distinct from those of NTP, both in their siting and coordination to the oxygens of the titanyl phosphate framework.

From the torsional energy of  $339 \text{ cm}^{-1}$ , an estimate of the rotational barrier can be made using the harmonic approximation and a simple cosine potential:

$$E^2 = \frac{\hbar^2 n^2 V_0}{2I}$$

Where  $E$  is the torsional energy,  $I$  the moment of inertia and  $V_0$  the height of the  $n$ -fold barrier. Taking an average value for the N-H bond length of  $0.1029 \text{ nm}$ , and assuming a fourfold barrier and  $90^\circ$  jump distances, so that  $n = 4$ , then an average barrier of  $14.5 \text{ kJ mol}^{-1}$  is obtained. A similar fourfold barrier has been observed previously for the halide salts. The calculated barriers for NTP and KNTF falls between those observed for the halide salts

where  $\text{NH}_4^+$  experience a strong barrier [4] and those where  $\text{NH}_4^+$  experience a weak potential as in the cages of zeolite rho [3]. It should be noted, however, that the different N-H...O bonds experienced by the  $\text{NH}_4^+$  ions in the titanyl phosphate actually precludes a symmetric fourfold potential, as experienced by the  $\text{NH}_4^+$  ions in the bcc ammonium halides, so that intercomparisons are only quantitatively useful.

The rotational barrier for NHTP may also be estimated from the torsional energy of  $323 \text{ cm}^{-1}$ , yielding a value of  $13.1 \text{ kJ mol}^{-1}$ , assuming  $n = 4$ . This supports the conclusion that the  $\text{NH}_4^+$  ions in NHTP are experiencing a weaker barrier to rotation than those in NTP and KNTF.

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## NEUTRON SPECTROSCOPIC STUDIES OF THE DYNAMICS IN SODALITES

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Inelastic incoherent neutron scattering experiments were performed for the first time on three members of the hydroxy-sodalite series  $\text{Na}_{6+x}[\text{AlSiO}_4]_6(\text{OH})_x \cdot n\text{H}_2\text{O}$  with the compositions  $x = 2, n = 0$  ("820 sodalite"),  $x = 2, n = 2$  ("822 sodalite"), and  $x = 0, n = 8$  ("608 sodalite") as well as on the corresponding deuterated equivalents. The framework  $\text{AlSiO}_4$  tetrahedra of these sodalites are alternatively connected via oxygen bridges forming a close-packed arrangement of  $\beta$  cages. The nonframework constituents Na, OH and  $\text{H}_2\text{O}$  are located inside this cage-like structure where they compensate the negative framework charge.

The sodalite structures have been studied by neutron and X-ray diffraction ([1] and references therein). For all three sodalites the sodium atoms are located on the edges of a tetrahedron in a structure averaged in space and time. In the 820 sodalite, the center of gravity of the OH lies in the center of the sodium cage. The oxygen of the water "molecules" in the 608 sodalite are located outside of the sodium tetrahedra on 8(e) positions and the corresponding hydrogen or deuterium atoms on 24(i) positions of the space group  $P43n$ . In this case, the 6 Na atoms are statistically distributed on the 8(e) positions. The 822 sodalite shows a much more

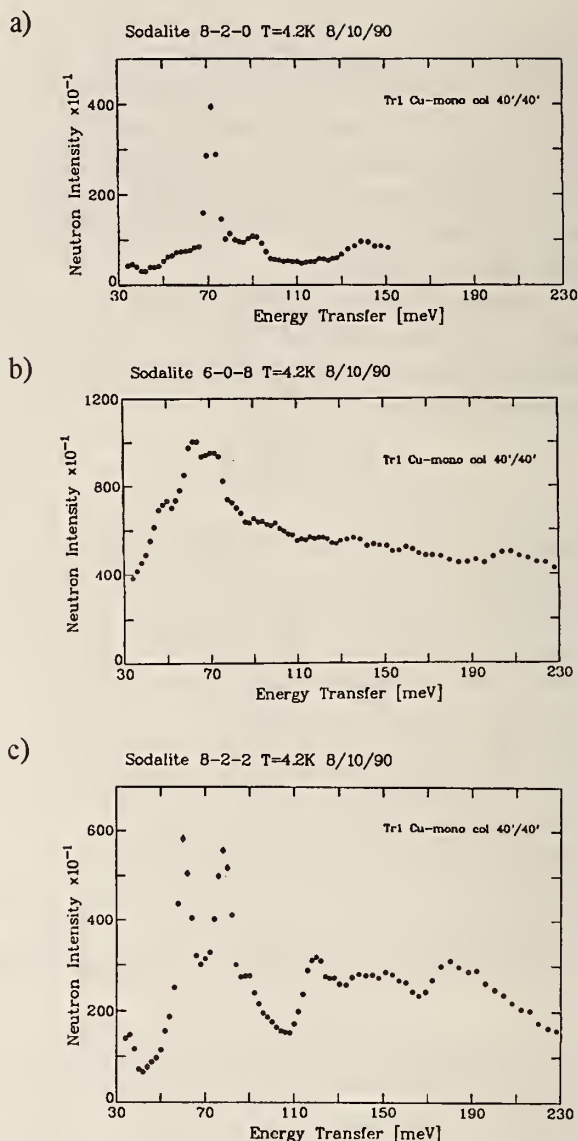
complicated structure involving a  $\text{H}_2\text{O}$ -HO complex rather than distinguished OH and  $\text{H}_2\text{O}$  molecules. This sodalite is the only one in the series studied which shows a phase transition (at 150 K). Only the high temperature structure could be well determined, and is much more complex than either of the other two sodalites. The structure is cubic but disordered and associates one hydrogen atom with a 8(e) position of the space group  $P43n$  near to the center of the sodium tetrahedra. The other hydrogen atoms and the oxygen atoms are statistically located on 8(e) and on 24(i) positions.

Inelastic neutron scattering data in the energy range 15-230 meV were collected at low temperatures in the range 4.2 - 12 K on the BT-4 spectrometer in the Be- and Be-graphite filter analyzer modes. One characteristic spectrum for each sodalite is shown in figure 1.

The well defined line at 72 meV in the spectrum of the 820 sodalite can be attributed to a local transversal vibration of the hydrogen [2]. Since the line at 90 meV is observed in each spectrum, it can be associated with an Al-O or Si-O stretching mode or with a combination of the mentioned transversal vibration with a low energy mode of the  $\text{Na}_4\text{-OH}$  complex. The contribution at 140 meV is likely an overtone of the 72 meV line.

The spectrum of the 608 sodalite exhibits a line at 210 meV, which can be attributed to the bending mode of the water molecules. Broad intensity contributions in the range 30-80 meV are assigned to stretching modes of the hydrogen bridges between the water oxygen and the framework oxygen. These modes are probably influenced by the absence of one sodium atom in each  $\beta$  cage. The importance of this absence is also demonstrated by recent results from quasielastic investigations, which showed rotational diffusion for only one water molecule [3].

Since the OH and the  $\text{H}_2\text{O}$  molecules cannot be distinguished, but are assumed to be a complex in the 822 sodalite, one cannot expect to observe a superposition of the 608 and the 820 spectra. Indeed, the measured 822 spectrum is far more complex. Intramolecular vibrations probably cause the observed spectral lines in the



**Figure 1.** Inelastic incoherent neutron intensities as function of energy transfer for a) 820 sodalite, b) 608 sodalite and c) 822 sodalite.

energy range above 110 meV. The two well-resolved lines between 50 and 110 meV are assigned to the collective vibrations of the  $\text{H}_3\text{O}_2$  complex. The line at 54 meV is an instrumental artifact.

A qualitative analysis of the dynamics in these sodalites is underway using the program CLIMAX [4]. This program uses the Wilson GF matrix method to calculate the vibrational frequencies and amplitudes and thus the corresponding neutron spectrum, which can be fitted directly to the observed data. Actually, it is unclear, whether or not this method of

resolving the dynamics of these sodalites is adequate. There are some indications that an approach which minimizes the energy in real potentials rather than one which adjusts force constants would be more successful. In the former case, one can in theory resolve the structure, the dynamics and the diffusion simultaneously.

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## STRUCTURE OF THE SODALITES $\text{Na}_{6+x}[\text{AlSiO}_4]_6(\text{OH})_2 \cdot n\text{H}_2\text{O}$ AND DEUTERATED ANALOGS

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Three members of the hydroxy-sodalite series  $\text{Na}_{6+x}[\text{AlSiO}_4]_6(\text{OH})_2 \cdot n\text{H}_2\text{O}$  with the compositions  $x = 2, n = 0$  ("820 sodalite"),  $x = 2, n = 2$  ("822 sodalite"), and  $x = 0, n = 8$  ("608 sodalite"), as well as the corresponding deuterated equivalents were the subject of a powder neutron diffraction study at various temperatures ranging from 4.2 K to 180 K. From previous studies [1,2] it is known that the aluminosilicate framework is completely ordered in the aluminosilicate sodalite phase. Recent neutron diffraction investigations [3,4,5] have found the structural positions of the nonframework constituents Na, OH,  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$ . For the 822 sodalite, a phase transition from the cubic disordered room temperature structure to the low temperature orthorhombic structure occurs at 150 K. No phase transitions were observed for the two remaining sodalites. These studies [3,4,5] showed rather large temperature factors for the nonframework constituents, which indicates, at least for the heavier atoms, possible static disorder. Furthermore, recent quasielastic neutron scattering measurements on the 820 sodalite have investigated the thermally activated jump diffusion [6] of the hydrogen atom, which occupies statistically one of the four possible positions in the  $(\text{Na}_4)$  tetrahedron. From these experiments a jump distance is found which is

significantly shorter than the corresponding values obtained from the neutron diffraction experiment [3]. The aim of the present neutron diffraction experiments was to reconsider the positions of the nonframework constituents in order to obtain better agreement with the observed diffusional and vibrational behavior of the studied sodalites.

Neutron diffraction measurements were carried out using the BT-1 diffractometer. Samples of the 820, 822, and 608 sodalites were synthesized by J. Felsche et al. The relatively low hydrogen concentration in the 820 and 822 sodalites, made these samples suitable for study without deuteration. For the 608 sodalite a deuterated sample was required, due to the high hydrogen concentration and the resulting background from the large hydrogen incoherent cross section. Due to only a partial deuteration of the 608 sodalite, no quantitative analysis of the structure could be performed. However, a measurement using a fully deuterated sample is currently in progress.

The neutron diffraction data of the deuterated 822 sodalite at 4.2 K and 180 K clearly showed the existence of two different phases, as found for the protonated sodalite [5]. While the high temperature diffractogram of the deuterated sample can be explained with the

structural model in [5] using the space group P43n, no agreement has been found for the low temperature phase, which is based on the space group P222.

Figure 1 shows the calculated, and measured neutron diffraction patterns of the protonated and the deuterated 820 sodalites. The new refinement of the structure (using program MINREF [7]) resulted in an modified view of the structure. The oxygen position of the OH group was found not to occupy the central position of the sodalite cage as suggested in earlier work [3]. On the contrary, both, the oxygen as well as the hydrogen atom of the OH group seems to be located statistically on the 8(e) positions of the space group P43n. In this case the center of gravity of the OH lies at the center of the sodalite cage. Furthermore, a smaller H-O distance of 0.096 nm was found for this new position, leading to a shorter length for the jump distance of the hydrogen atom. This seems to be compatible with the new quasielastic measurements. As indicated by the remaining discrepancies between the calculated and the observed neutron diffractograms (in particular for the deuterated 820 sample), further modifications of the structural model are needed. The introduction of a possible trigonal deformation of the sodium cage, which is correlated with the position of the hydrogen atom on one of the sides of the sodium cage faces, leads to a refinement with the space group R3c. In fact, it is not possible to distinguish between a undeformed and a deformed sodium cage. So, the trigonal deformation can not be

excluded. Such a deformation would give the preference for a two-site model for the rotational diffusion of the hydrogen, which is also reflected in the quasielastic data. Further refinements and measurements are in progress.

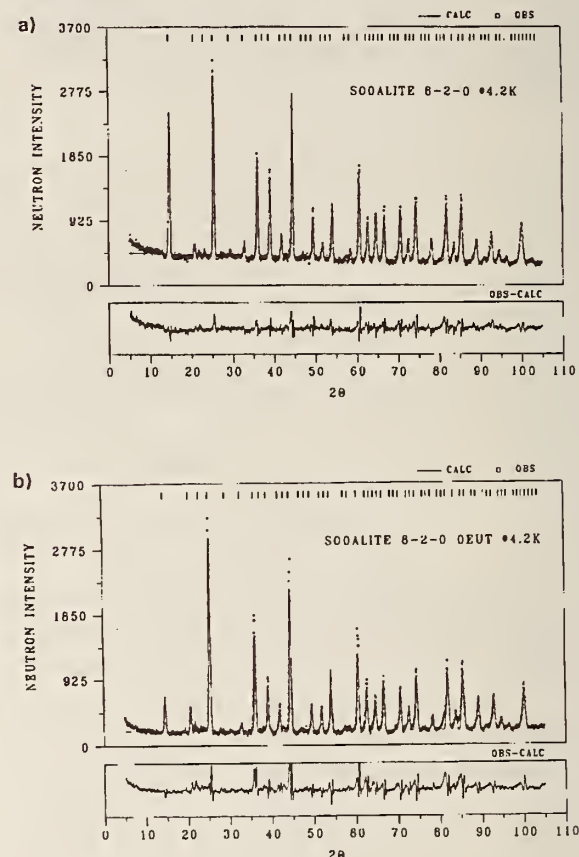


Figure 1. Observed and calculated neutron diffraction pattern of a)  $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2$  and of b)  $\text{Na}_8[\text{AlSiO}_4]_6(\text{OD})_2$  at 4.2 K.

Table 1. Structure parameter of  $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2$  at 4.2 K

Lattice constant:  $a = 0.8737(1)$  nm

Space group: P43n (undeformed Na cage)

Refinement Factors:  $R_{\text{weighted profile}} = 0.096$ ,  
 $R_{\text{profile}} = 0.075$   
 $R_{\text{expected}} = 0.045$

Atom	Pos.	X	Y	Z	n	$B_{\text{iso}}$
Al	6(c)	0.250	0.500	0.000	1.00	1.1
Si	6(d)	0.250	0.000	0.500	1.00	1.1
O1	24(i)	0.137	0.428	0.147	1.00	1.1
O2	8(c)	0.013	0.013	0.013	0.25	2.6
H	8(c)	-0.051	-0.051	-0.051	0.25	2.8
Na	8(c)0.159		0.159	0.159	1.00	1.9

Space groups: R3c (deformed Na cage)

Refinement Factors:  $R_{\text{weighted profile}} = 0.104$ ,  
 $R_{\text{profile}} = 0.082$ ,  
 $R_{\text{expected}} = 0.047$

Atom	Pos.	X	Y	Z	n	$B_{\text{iso}}$
Al	6(b)	0.250	0.500	0.000	1.00	0.44
Si	6(b)	0.250	0.000	0.500	1.00	0.44
O1	6(b)	0.137	0.428	0.144	1.00	0.44
O2	6(b)	-0.137	-0.428	0.144	1.00	0.44
O3	6(b)	-0.137	0.428	-0.144	1.00	0.44
O4	6(b)	0.137	-0.428	-0.144	1.00	0.44
Na1	2(a)	0.178	0.178	0.178	1.00	1.23
Na2	6(b)	-0.157	-0.157	0.157	1.00	1.23
O5	2(a)	0.010	0.010	0.010	1.00	2.27
H	2(a)	-0.054	-0.054	-0.054	1.00	2.47

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## STRUCTURES AND PROPERTIES OF NEW ZEOLITE X-TYPE BERYLLOPHOSPHATE AND ZINCOPHOSPHATE MOLECULAR SIEVES

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The solid state chemistry of nonaluminosilicate molecular sieves has recently undergone a renaissance, following the discovery of a number of phases in which framework aluminum and silicon are replaced by phosphorus, gallium and beryllium. Some of these AlPOs, GaSiOs, and BePOs are isostructures of known aluminosilicates, while others have new framework topologies. We have recently characterized the structures of the new beryllorphosphate (BePO-X) and zincophosphate (ZnPO-X) phases that are analogues of the industrially important zeolite-X framework using neutron and x-ray diffraction [1]. Zeolite-X is a synthetic isostructure of the mineral faujasite. Faujasite-type phases contain one of the largest pore openings of any known zeolite (ca. 8 Å) and are of industrial importance for petroleum cracking and other reactions [2].

BePO-X ( $\text{Na}_{96}(\text{BePO}_4)_{96} \cdot 192\text{H}_2\text{O}$ ) and ZnPO-X ( $\text{Na}_{67}\text{TMA}_{12}\text{Zn}_8(\text{ZnPO}_4)_{96} \cdot 192\text{H}_2\text{O}$  (TMA = Tetramethylammonium cation)) were prepared at ambient conditions [3]. For BePO-X, a sample was dehydrated under vacuum at 150 K overnight and sealed in a vanadium can. The data were collected, with the sample at 10 K, using the high resolution five-detector powder diffractometer at NIST. For ZnPO-X, high resolution powder x-ray data were collected on a Scintag PAD X diffractometer.

Rietveld profile refinement was carried out with the program GSAS [4], using the starting framework model of aluminosilicate zeolite-X [5], space group  $Fd\bar{3}$  (No. 203). Our BePO-X and ZnPO-X models assumed a fully ordered 1:1 distribution of Be/Zn and P over the framework tetrahedra, and strict alternation of Be/Zn and P between adjacent tetrahedra, as would be the case for an X-type zeolite with a 1:1 Si:Al ratio, showing perfect cation alternation. For each phase the usual profile parameters were refined. For BePO-X, Na cations were positioned at the sites found in previous studies of dehydrated faujasite-type materials. For ZnPO-X, extra framework species were progressively located by difference Fourier syntheses and added to the refinement. The largest difference peaks were assigned to sodium cations and those remaining to extraframework water molecules. No reasonable geometry corresponding to the tetramethylammonium guest cation could be established. For both BePO-X and ZnPO-X, the occupancies and thermal factors of the guest were refined to ensure convergence to the best possible minimum. No bond-distance restraints were employed for the BePO-X refinement. The final cycle of least-squares calculations converged to give residuals of  $R_p = 6.20\%$  and  $R_{wp} = 8.17\%$  ( $\chi^2 = 1.96$ ) for 67 variable parameters and 3495 observations. The final atomic positional parameters for BePO-X are listed in table 1,

with selected bond distances/angle data in table 2. The final observed, calculated and difference profiles for one detector are illustrated in figure 1. For ZnPO-X, residuals of  $R_p = 7.23\%$  and  $R_w = 9.25\%$  ( $\chi^2 = 6.29$ ) for 45 variable parameters and 3002 observations were obtained. Final atomic positional parameters and selected bond distances/angle data for ZnPO-X are given in ref. 1, together with details of MAS NMR, thermogravimetric and analytical results for both samples.

These new BePO-X and ZnPO-X phases crystallize in the faujasite-type zeolite X structure, which consists of cuboctahedral sodalite ( $\beta$ ) cages linked via 6-rings or hexagonal prisms in a diamond-like array that surrounds large supercages. The framework consists of 1 Zn/Be atom and 1P and 40 atom sites, all on general crystallographic positions. The framework atom's unit cell content is  $(\text{Zn/Be})_{96}\text{P}_{96}\text{O}_{384}^{96-}$ , with charge compensation provided by the extra framework species: for BePO-X sodium cations and for ZnPO-X, sodium, TMA and possibly zinc cations.

For BePO-X, the framework-atom geometry is in good accordance with the expected behavior of these species ( $d_{av}(\text{Be-O}) = 1.61(5) \text{ \AA}$ ,  $d_{av}(\text{P-O}) = 1.55(6) \text{ \AA}$ ). The three distinct locations for the sodium atoms, all on the body diagonal of the cubic cell, are similar to those found in studies of dehydrated sodium aluminosilicate-X phases [5]. The total unit-cell occupancy of the  $S_I$ ,  $S_{I'}$  and  $S_{II}$  is ca. 63, leaving 33 sodium atoms unaccounted for. No other significant site populations were established from Fourier maps, suggesting that the other sodiums may be dispersed over a number of sites in the supercage.

Table 1. Final Atomic Coordinates for BePO-X (Cubic, Space Group  $Fd\bar{3}$ ,  $a = 23.368(2) \text{ \AA}$ )

Atom	x	y	z	occ <sup>a</sup>	100U <sub>iso</sub>
Be(1)	-0.0525(6)	0.1247(7)	0.0357(6)	1.1(2)	
P(1)	-0.0547(8)	0.0370(8)	0.1226(10)	1.1(2)	
O(1)	-0.1071(6)	0.0071(6)	0.1043(6)	1.1(2)	
O(2)	-0.066(6)	-0.0013(6)	0.1477(4)	1.1(2)	
O(3)	-0.0279(4)	0.0687(7)	0.0694(7)	1.1(2)	
O(4)	-0.0730(5)	0.0768(8)	0.1740(7)	1.1(2)	
Na(1)	0	0	0	1.08(7)	2.8(6)
Na(2)	0.067(2)	0.067(2)	0.067(2)	0.47(4)	2.8(6)
Na(3)	0.2442(6)	0.2442(6)	0.2442(6)	1.04(7)	2.8(6)

<sup>a</sup>Fractional site occupancy

Table 2. Selected Bond Distance (angstroms) and Angle (degrees) Data for BePO-X

Be(1)-O(1)	1.62 (3)	Be(1)-O(2)	1.64 (3)
Be(1)-O(3)	1.63 (3)	Be(1)-O(4)	1.55 (3)
P(1)-O(1)	1.47 (3)	P(1)-O(2)	1.55 (3)
P(1)-O(3)	1.58 (4)	P(1)-O(4)	1.58 (3)
Na(1)-O(3)	2.372 (8) x 6	Na(2)-O(3)	2.22 (3) x 3
Na(3)-O(2)	2.28 (2) x 3		
O-Be(1)-O <sup>a</sup>	109 (2)	O-P(1)-O <sup>a</sup>	110 (4)
Be(1)-O-P(1) <sup>b</sup>	136 (2)		

<sup>a</sup>Tetrahedral average. <sup>b</sup>Bridging oxygen average.

These new BePO-X and ZnPO-X phases are representatives of an extensive new class of zeolite materials not based on group IIIa or group IVa metal atom framework compositions. Further work on the preparation, modification and characterization of these and related systems is in progress.

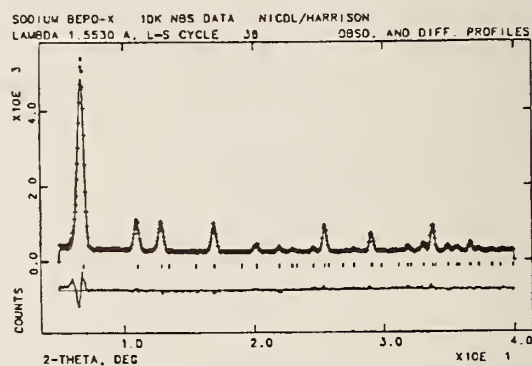


Figure 1. Final observed (crosses), calculated (line), and difference profile plots, with reflection positions indicated by tickmarks for BePO-X (first detector, low-angle neutron data).

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**Sr<sub>2</sub>Bi<sub>2</sub>O<sub>5</sub>: A STRUCTURE CONTAINING ONLY 3-COORDINATED BISMUTH**

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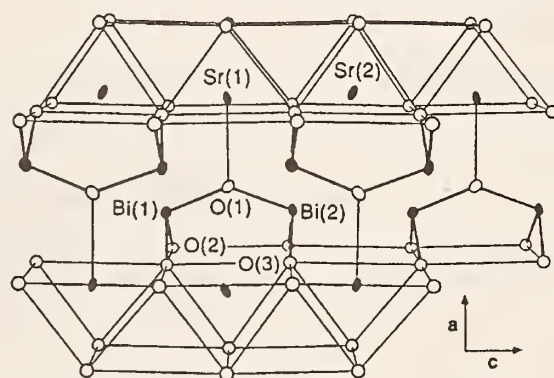
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The bismuth (III) strontium oxide Sr<sub>2</sub>Bi<sub>2</sub>O<sub>5</sub> has been synthesized in the low-temperature form, and studied using single-crystal x-ray and powder neutron diffraction techniques. The compound crystallizes with the symmetry of space group Pnma with  $Z = 4$  and x-ray lattice parameters  $a = 14.261(3)$ ,  $b = 6.160(2)$ ,  $c = 7.642(3)$  Å. All bismuth ions are in threefold coordination with oxygen and form ...Bi(1)-O(1)-Bi(2)...□...Bi(1)-O(1)-Bi(2)...chains propagating in the direction of the c-axis, as shown in figure 1 (the symbol □ indicates an oxygen vacancy). These chains are stacked along the a-axial direction and are connected by Bi-O bonds between the Bi ions in the chains and oxygen ions in the Sr-O slabs, and by Sr-O bonds between the Sr(1) ions in the slabs and O(1) atoms in the chains. Strontium is seven-coordinated to six oxygen ions forming a trigonal prism and to one oxygen ion belonging to the chains. The Bi ions along the chain are not evenly spaced, thereby contributing to a "superstructure", along the c-axial direction, observed in long exposure precession photo-

graphs. The geometry around the bridging oxygen ion O(1) is trigonal planar because the four atoms Bi(1), Bi(2), Sr(1), and O(1) lie on the same mirror plane. There are no bonds to O(1) out of the mirror and O(1) can therefore vibrate more or less freely in the direction perpendicular to the plane.



**Figure 1.** Representation of the structure of Sr<sub>2</sub>Bi<sub>2</sub>O<sub>5</sub>. The filled circles indicate the Bi and Sr ions. The Sr-O slabs and the Bi-O chains are connected by Sr(1)-O(1) bonds.

**THE CRYSTAL STRUCTURE OF A DEFECT PYROCHLORE, NaW<sub>2</sub>O<sub>6.5</sub> · D<sub>2</sub>O**

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and

E. Prince

Neutron powder diffraction and Rietveld refinement [1] were used to refine the crystal structure of a deuterated sample of a defect pyrochlore with the composition NaW<sub>2</sub>O<sub>6.5</sub> · D<sub>2</sub>O. This compound crystallizes in the space group Fd3m, with the lattice parameter  $a = 10.3125(2)$  Å. The structure is built from slightly distorted WO<sub>6</sub> octahedra that share corners to form a three dimensional framework.

This rather rigid framework determines the overall crystal structure. It contains a set of hexagonal channels that intersect, forming substantial sized cavities, but their sizes and shapes are not particularly well suited to accommodating the additional oxygen, the sodium atoms, and the water molecules. As a result the remaining structure is highly disordered, with no one crystallographic site

being more than half full, and some of the deuterium occupying only six out of 192 equivalent sites of a general position. The coordinates and occupancies of the structure that gives the best fit to the data ( $R_{wp} = 6.58\%$ ,  $R_E = 5.30\%$ ,  $R_B = 9.88\%$ ) are given in table 1.

Table 1. Parameters for  $\text{NaW}_2\text{O}_{6.5} \cdot \text{D}_2\text{O}$ . Space group  $\text{Fd}3\text{m}$

Atom	site	x	y	z	B	N
W	16c	0	0	0	0.8(2)	1.0
O1	48f	0.3125(5)	1/8	1/8	0.6(1)	1.0
O2	32e	0.4073(8)	x	x	1.7(5)	0.385(1)
Na	16d	1/2	1/2	1/2	1.0	0.5(2)
D1	192i	0.404(6)	0.195(4)	0.137(6)	1.0	0.028(2)
D2	96g	0.902(2)	x	0.476(3)	1.0	0.13(1)

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## THE CRYSTAL STRUCTURE OF $\text{Na}_x\text{WO}_{3+x/2} \cdot y\text{H}_2\text{O}$

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Neutron powder diffraction and the Rietveld [1] method were used to refine the crystal structure of a synthetic tungstate with the composition  $\text{Na}_{0.17}\text{WO}_{3.085} \cdot y\text{H}_2\text{O}$ . Two samples were used, a protonated sample with  $y = 0.19$  and a deuterated sample with  $y = 0.23$ . This compound crystallizes in a structure that is closely related to hexagonal tungsten bronze (HTB), which consists of a framework of corner-sharing  $\text{WO}_6$  octahedra, but differs from HTB in that layers perpendicular to the  $c$  axis are flat (space group  $\text{P}6/\text{mmm}$ ) rather than puckered (space group  $\text{P}6_3/22$ , with a doubled  $c$  axis). As is shown in figure 1, the octahedra form six membered rings, leading to hexagonal channels running through the crystal parallel to the  $c$  axis. The alkali cation and the extra oxygen, some of which is water, reside in these channels, which is somewhat surprising, because oxygen and water apparently diffuse in and out rather easily although there would seem to be insufficient space for the atoms and molecules to pass the cations.

The initial data were collected on the sample prepared in natural water, but, because of the high background due to incoherent scattering from the protons, the data proved to be difficult to interpret. Another sample was therefore prepared using heavy water, and a second data set was collected. The structure was successfully refined from these data to  $R_{wp} = 6.38\%$  ( $R_E = 5.81\%$ ),  $R_B = 9.02\%$ . Table 1 gives the final structural parameters.

After refinement of the deuterated data the protonated data set also refined satisfactorily, confirming that the peaks that had been assigned to deuterium were indeed parts of water molecules. There is not enough room for sodium atoms to occupy more than half of the positions assigned to them. The lack of a doubled unit cell is probably due to disorder such that there is no correlation from one channel to another determining which half of the positions is occupied.

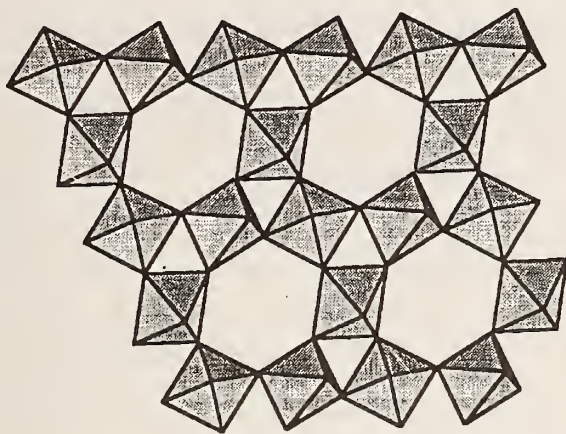


Figure 1. The arrangement of corner shared  $\text{WO}_6$  octahedra in hexagonal tungsten bronze.

Table 1. Refined parameters for  $\text{Na}_{.17}\text{WO}_{3.085} \cdot 0.23 \text{H}_2\text{O}$

Space group  $\text{P6}/\text{mmm}$ ,  $a = 7.329(2) \text{ \AA}$ ,  $c = 3.891(1) \text{ \AA}$

Atom	Site	x	y	z	B	Occupancy
W	3f	0.5	0.0	0.0	3.8(4)	1.0
O1	3g	0.5	0.0	0.5	1.5(1)	1.0
O2	6l	0.2114(4)	2x	0.0	1.2(1)	1.0
O3	2e	0.0	0.0	0.412(4)	2.6(8)	0.5
D	12a	0.071(3)	2x	0.312(7)	1.0	0.095

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## STRUCTURE OF Mg-EXCHANGED BePO-X

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and

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Recently, new analogues of zeolite-X containing beryllium/zinc and phosphorus as the framework tetrahedral atoms have been described [1]. Here we report the crystal structure of a magnesium-exchanged beryllophosphate-X phase (Mg-BePO-X). The preparation of the BePO-X phase has been described previously [2].

The new Mg-BePO-X (cubic,  $a = 23.2423(8) \text{ \AA}$ , space group  $Fd\bar{3}$ ) crystallizes in the faujasite-type zeolite-X structure. This structure consists of cuboctahedral sodalite or  $\beta$ -cages linked via double 6-rings or hexagonal

prisms in a diamond like array. The framework surrounds large 'supercages', which correspond to about 50% 'empty space' in volume percentage, as described previously [1]. The framework consists of 1 Be atom, 1 P and 4 O atom sites, all on general crystallographic positions. The framework atoms' unit cell content is  $\text{Be}_{96}\text{P}_{96}\text{O}_{384}^{96-}$ , with charge compensation provided by the extra-framework magnesium cations.

For Mg-BePO-X, the framework-atom geometry is in good accordance with the expected behavior for these species ( $d_{\text{ave}}(\text{Be-O})$

$= 1.61 \text{ \AA}$ ,  $d_{ave}(\text{P-O}) = 1.54 \text{ \AA}$ ). Two distinct locations were found for the magnesium cations, both on the body diagonal of the cubic cell. The first, at the origin, is approximately octahedrally coordinated by O(3) ( $d(\text{Mg-O}(3)) = 2.133(4) \text{ \AA}$ ), and is located in the center of the hexagonal prism joining adjacent  $\beta$ -cages ( $S_I$  site). This site is fully occupied and illustrated in figure 1. The  $S_{II}$  position ('free' 6-ring joining the  $\beta$ - and supercages), is about 50% occupied with three Mg-O(2) bond lengths of  $2.170(7) \text{ \AA}$ , in pyramidal configuration (fig. 2). Other magnesium cation sites are probably in the supercages.

Further studies on other ion-exchanged species and other new zeolite analogues are now in progress.

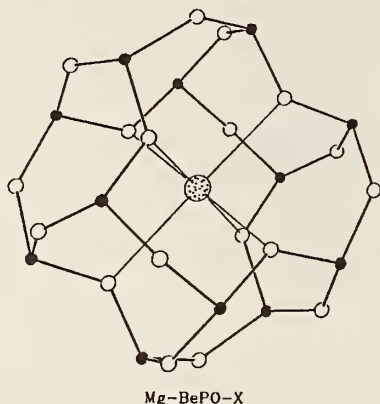


Figure 1. ORTEP view of the double 6-ring window in magnesium-exchanged beryllophosphate zeolite-X. Be/P atoms filled circles, O atoms plain, Mg cation speckled. The Mg(1) cation is octahedrally coordinated (thin lines) by oxygen atoms.

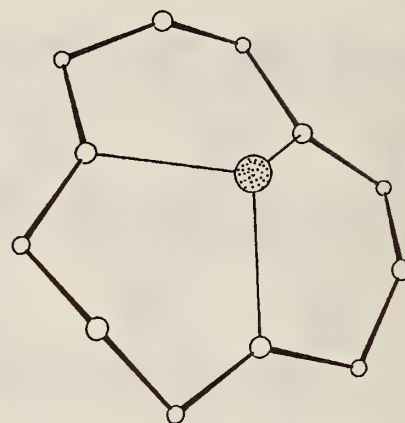


Figure 2. ORTEP view of the Mg(2) site in Mg-BePO-X. The pyramidally-coordinated  $\text{Mg}^{2+}$  protrudes into the supercage.

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## STRUCTURE OF LITHIUM CHABAZITE

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The aluminosilicate zeolite chabazite (typical formula:  $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 12\text{H}_2\text{O}$ ) has a structure based on 8-rings, double 6-rings and 4-rings. It may be visualized as ABC-stacks of double 6-rings joined through slanted 4-rings, leading to large cavities, interlinked by a 3-d network of 8-rings. Typical zeolitic cation exchange is

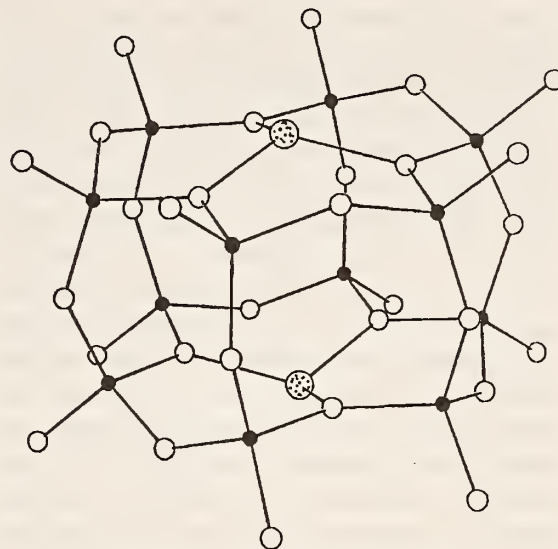
possible, and several structural studies have been made on chabazites containing various guest cations and/or waters of hydration.

Li-exchanged chabazite (Li-CHA) is structurally most similar to dehydrated cupric chabazite [1] in terms of guest cation configuration and framework distortion. The structure of

Li-CHA was determined by Rietveld refinement using low-temperature neutron powder data collected on the high resolution five-detector diffractometer BT-1 at NIST. The starting framework model was in space group  $R\bar{3}m$  (No. 166) and the final cell dimensions were  $a = 9.3354(8) \text{ \AA}$ ,  $\alpha = 93.677(5)^\circ$ . No evidence for a monoclinic distortion was observable.

The guest  $\text{Li}^+$  cation was located from difference Fourier syntheses, following refinement of the framework atoms, and the usual profile parameters. One confirmed lithium site was found, on the  $[111]$ -body diagonal: lithium sits in trigonal coordination (site symmetry  $3m$ ) with three bonds to O(4) of  $1.948(11) \text{ \AA}$  (fig. 1). The structure of cupric chabazite [1] is most similar to the phase described here.

The framework of Li-CHA appears to be the most distorted chabazite determined to date. The degree of distortion of the  $\text{TO}_4$  tetrahedron (where  $T = \text{Si}$  or  $\text{Al}$ ) leads to a very large  $\text{T-O(2)-T}$  bond angle, linking double-6 rings ( $173.6(8)^\circ$ ). The  $\text{T-O(4)-T}$  bond angle reduces to  $124.0(7)^\circ$ , reflecting the lithium coordination of this oxygen ( $d(\text{T-O}) = 1.715(9) \text{ \AA}$ ). The average  $\text{T-O}$  bond distance of  $1.645 \text{ \AA}$  is in good agreement with other studies and in accordance with the  $\text{Si:Al}$  ratio in chabazite.



Chabazite -- double 6-ring

**Figure 1.** ORTEP view of the double 6-ring window in Lithium-exchanged Chabazite: silicon/aluminium atoms filled circles, oxygen atoms plain, lithium cations speckled. The pyramidally-coordinated  $\text{Li}^+$  cations occupy the outer face of the 6-ring windows.

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## THE LOW TEMPERATURE CRYSTAL STRUCTURE OF ACETONITRILE

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Acetonitrile ( $\text{CH}_3\text{CN}$ ) presents a possibly very interesting candidate molecule for the study of methyl rotational properties in the solid state. The absence of substantial intramolecular interactions contributing to the definition of the methyl rotational potential leads to an expectation of a low barrier produced by intermolecular interactions. A previous determination of the low temperature structure has been reported [1]. This study was obtained at  $100 \text{ K}$  with data of limited quality from which, in particular, the thermal parameters for the deuterium atoms were reported only in the isotropic approximation. It is for the purpose of

verifying the structure and obtaining anisotropic deuterium thermal parameters that the present study was undertaken.

The preparation of a good quality powder sample was accomplished by grinding the sample in a mortar and pestle cooled by placing on solid  $\text{CO}_2$ . The sample was quickly transferred to a cold cryostat to prevent a temperature rise. No care was taken to follow the procedure suggested in ref. [2] to ensure the existence of the low temperature phase. The absence of preferred orientation was verified by observing a constant intensity of a strong diffraction peak as a function of sample orientation and the presence

of a single phase by the success of the refinement. The diffraction pattern were obtained from the powder diffractometer BT-1 at a sample temperature of 4.2 K. The 100 K structure reported by Antson et al. [1], was used for the initial model of the refinement. With the anisotropic thermal parameter assigned to each atom, the final refinement converged to  $R_B = 2.67$ ,  $R_P = 4.79$ ,  $R_{WP} = 6.63$  for  $R_e = 5.32$ . The molecule is positioned on the mirror plane with the three nonhydrogenous atoms and D1 on the mirror plane. The molecular axis, C1-C2 $\equiv$ N, has a true linear form within the experimental error ( $179.6(5)^\circ$ ). The three C-D bonds of the methyl group are arranged in the normal tetrahedral form with the deviation less than  $2^\circ$  in bond angles. The bond angles are given in table 1. The thermal ellipsoids of the D atoms were about twice larger than those of the C and N atoms, and their orientations were consistent with the molecular libration motion. The rigid body motions (T L and S) obtained from the atomic thermal motions by the method of Schomaker and Trueblood are shown in table 2. The largest librational motion occurs about the molecular axis with the r.m.s.

amplitude of about  $6^\circ$ . This small value suggests a large rotational barrier.

**Table 1.** The bond-lengths and bond-angles of CD<sub>3</sub>CN at 10 K

Bond lengths (Å):		Bond angles (°):	
C1 - C2	1.460(5)	C1-C2-N	179.6(5)
C2 - N	1.159(5)	D1-C1-C2	109.5(4)
C1 - D1	1.109(6)	D2-C1-C2	109.6(3)
C1 - D2	1.079(3)	D1-C1-D2	108.3(4)
		D2-C1-D2'	111.4(5)

**Table 2.** T(i,j) and L(i,j) elements of the rigid body motions

	T(i,j) (Å <sup>2</sup> ):	L(i,j) (sq. rad.):
11	0.0083(39)	0.0022(21)
22	0.0122(25)	0.0078(52)
33	0.0095(33)	0.0074(61)
12	0.0000	0.0000
13	0.0000	0.0000
23	-.0031(25)	-.0024(24)

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## PHASE DETERMINATION FOR MACROMOLECULAR X-RAY DIFFRACTION DATA BY MAXIMUM ENTROPY

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and  
E. Prince

Because of the interesting results obtained in a trial of determining the phases of X-ray diffraction intensities by the use of maximum entropy [1,2], a further trial was begun with data taken from crystals of a protein whose structure was unknown. This protein, bovine heart creatine kinase, or BHCK, has 381 amino acid residues in its molecule. Pairs of molecules bond together to form dimers in crystals that belong to space group  $P4_22_12$ , with unit cell dimensions  $a = 132.4 \text{ Å}$ ,  $c = 74.9 \text{ Å}$ . Consideration of density determines that there is one monomer in the asymmetric unit, and it is reasonable to assume that the two halves of the

dimer are related by a twofold rotation axis. Because the monomer must be asymmetric, the other twofold axes in the unit cell cannot pass through it, which makes it probable that the twofold rotation that is a subgroup operation of the  $4_2$  screw axis is the symmetry axis of the dimer.

A first step in the trial was to refine the computer program to utilize fast fourier transforms [3] that exploit the space group symmetry [4,5] to reduce memory requirements and optimize speed of execution. In this space group the density map needs to be computed in only one eighth of the unit cell, and only one

sixteenth of the structure factors need to be computed.

In  $P4_22_12$  all  $hk0$  and  $hh\ell$  reflections must be real, and those of  $h0\ell$  may be real or imaginary, but may not be complex. The phases of one  $hk0$  reflection with  $h + k$  odd and one  $hh\ell$  reflection with  $\ell$  odd may be chosen arbitrarily to define the origin, and that of one  $h0\ell$  reflection that has an imaginary structure factor may be chosen to determine the enantiomorph. Phase determination proceeded in two steps. First the unit cell was divided into pixels  $\sim 2$  Å on a side, and a subset of the data was selected with  $d$  spacings no shorter than 5 Å. The strongest reflection from each class was chosen to fix the origin and enantiomorph. The phases of 240 additional reflections from the three central classes were chosen, in blocks of 16, by a systematic search for the sign combination that gave the map with the highest entropy. Reflections with general phases were added, one at a time, by trying phases in steps of  $20^\circ$  from  $0^\circ$  to  $340^\circ$  and fitting the amplitudes, again searching for the maximum entropy map.

When phases for reflections in this low resolution subset had been determined ( $R < 3.0\%$ ) a new map was computed using this same subset of reflections but with pixels 1 Å on a side. The entire data set (28164 reflections) was then added to the map following the same procedure as before. Finally, a map was calculated and analyzed by a program that traces ridge lines in the density, and both density and ridge line traces were displayed on a computer graphics system.

Because of the configuration of symmetry elements in the unit cell, it was probable that most of the monomeric molecule would lie in a region from  $z = 0$  to  $z = 1/2$  and either from  $x = 0$  to  $x = 1/2$  and  $y = 1/4$  to  $y = 3/4$  or from  $x = 1/4$  to  $x = 3/4$  and  $y = 0$  to  $y = 1/2$ , but the choice between these two is determined by the arbitrary choice of origin. A region of the unit cell from 0 to  $1/2$  in all three dimensions should contain  $1/2$  of each of two molecules. When the ridge tracing of this region was displayed, a division between two molecules was clearly visible. A portion of the unit cell was then calculated that contained one molecule, and the ridge tracing and density were examined for features of secondary structure commonly found in proteins. There are several regions that are fit by  $\alpha$ -helices, all winding in the same direction, and also regions fit by  $\beta$ -sheets up to five strands wide. Work on interpretation of the map is continuing.

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## EXPLOITING SYMMETRY IN CRYSTALLOGRAPHIC FAST FOURIER TRANSFORMS

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 and  
 E. Prince

The interpretation of X-ray and neutron diffraction data requires extensive use of Fourier transforms. A discrete Fourier transform (DFT) can be represented as a multiplication of a vector of  $N$  elements, often complex, by an  $N \times N$

matrix, most of whose elements are complex. A fast Fourier transform (FFT) is formed by factoring this dense matrix, by one or a combination of many different techniques [1], into a product of sparse matrices, thus reducing

the computation from one requiring a number of computations approximately proportional to  $N^2$  to one requiring a number of computations approximately proportional to  $N \log N$ , which increases only slightly faster than linearly as  $N$  increases. In crystallographic computations, space group symmetry can be used to reduce execution time and storage requirements still further [2]. Crystallographic computations also possess other special properties, such as the fact that electron densities are real numbers, so that their transforms are Hermitian, or the fact that, when  $2_1$  screw axes are present, data points that are one half of a period apart are complex conjugates of one another.

Fourier transforms in two or more dimensions can be performed by sequences of 1-d transforms, (the row-column method) so computer code is needed only for the 1-d transforms. Because methods that can be adapted to some of the special conditions found in crystallography are most efficient if the

number of subdivisions in a period is two or four times an odd number, transforms are needed for odd as well as even number of points. A library of subroutines has been written in Fortran 77 for all even number of points from 20 to 200 and all odd number of points from 11 to 99 that have no prime factors larger than 17. Additional subroutines have been written that provide efficient computation of transforms from real or Hermitian data and data possessing other kinds of symmetry. Subroutines that exploit the symmetries of six frequently occurring space groups have also been written. This list is being extended to include twenty-one space groups to which more than 80% of observed protein structures belong.

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## NIST\*LATTICE—DETERMINATION AND CRITICAL EVALUATION OF SYMMETRY

V. L. Karen and A. D. Mighell

NIST\*LATTICE [1] has been completed and is ready for distribution to the scientific community. The program is written in standard FORTRAN and can be used in any diffraction or analytical laboratory. The software is multi-functional and can be used to analyze various types of lattice relationships. The present version of the NIST\*LATTICE performs several functions including: 1) the determination of symmetry and the evaluation of experimental error; 2) the generation of transformation matrices relating any two unit cells; 3) the calculation of the reduced cell of a lattice, and the calculation and reduction of specified derivative supercells and/or subcells; and 4) unit cell transformations. The program has many applications in the analytical and material sciences including phase characterization, materials design, and symmetry determination.

The Symmetry Program Function in NIST\*LATTICE is extremely reliable for the determination of crystal symmetry as it can calculate groups of symmetry matrices with respect to any specified cell no matter how skewed. In sharp contrast to commonly used techniques, the program allows one to determine all symmetries and pseudosymmetries, to evaluate experimental error taking into account all the lattice symmetry operations, and to calculate exactly where to look for equivalent hkl's regardless of the reference system [2,4].

During the year, the program has been used to evaluate the crystal symmetry of compounds reported in a number of leading journals. It has been found that it is not uncommon for the crystal to be assigned the wrong space group. This is true for small molecules as well as for proteins [3]. To prevent such errors in the published literature, we have taken several steps.

First, we have installed the program in the Technical Office of Acta Crystallographica in Chester, England so that all structures can be checked for the correctness of symmetry prior to publication. Second, the program along with a Technical Manual [1] will be distributed to the scientific community so that one can check the symmetry at any stage of an analysis. Finally, it is planned to incorporate the code directly into commercial diffractometers so as to automate, for the first time, the entire data collection process in a logical and reliable manner.

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## NIST CRYSTAL AND ELECTRON DIFFRACTION DATA CENTER

A. D. Mighell and V. L. Karen

The NIST Crystal and Electron Diffraction Data Center is concerned with the collection, evaluation, and dissemination of data on solid-state materials. The Data Center maintains a central database with chemical, physical, and crystallographic information on all types of well-characterized substances. These materials fall into the following categories: inorganics, organics, organometallics, metals, intermetallics and minerals. During this year, the master database has been significantly augmented with respect to all categories of materials and now contains greater than 170,000 entries. From this central database, two distribution databases are produced: NIST CRYSTAL DATA [1] and the NIST/sandia/ICDD Electron Diffraction Database [2].

These databases are made available to the scientific community through computer oriented modes of dissemination including: magnetic tape, on-line searching, CD-ROM, and scientific instruments. Recent developments and applications with respect to these distribution modes are briefly discussed below.

**Magnetic Tape.** In the Spring of this year, search software and the database were installed in the Technical Office of Acta Crystallographica in Chester, England. Using lattice-matching techniques, each 'new' structure can routinely be checked against the database to see if the compound, or related structure, has been previously studied. As research in the Data Center has proved that the lattice/element-type

combination uniquely characterizes a material, this type of check by the journal editors will prevent unwanted multiple publication of the same compound.

**On-Line Searching.** The online system for NIST CRYSTAL DATA, known as CRYSTDAT [3], consists of the database along with search and analysis software. Recently, CRYSTDAT has been upgraded to include data on 183,000 crystalline compounds. The system has been significantly expanded to include over 26 million searchable parameters. New search tools that are based on Boolean logic have been added. CRYSTDAT is ideal for analytical purposes, materials research, and statistical studies. For example, statistical analyses of space group frequencies for various classes of materials have been carried out and the results will be published in 1992.

**CD-ROM.** A CD-ROM containing three databases on the same disk is now being distributed. These databases are: NIST CRYSTAL DATA, the NIST/sandia/ICDD Electron Diffraction Database and ICDD Powder Diffraction File. This product is being marketed by the International Centre for Diffraction Data. In August, a workshop was organized at the PIXAM International Diffraction Conference on the combined use of these three databases for phase characterization using x-ray, neutron, and electron diffraction data.

**Scientific Instruments.** Throughout 1990/1991, we have visited a series of manufacturers

of commercial analytical electron microscopes and single-crystal x-ray diffractometers. Our objective is to integrate the database directly into the instrument to permit identification as soon as lattice and chemical data are known. To facilitate use of the database in this mode, a comprehensive manual of relevant papers on phase characterization has been prepared by the Data Center. To date, the database along with search software have been integrated into several commercial instruments.

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- [3] CRYSTDAT(1991). An International Online Search System for NIST CRYSTAL DATA. Developed jointly by the Canada Institute of Scientific and Technical Information (John R. Rodgers) and the NIST Crystal Data Center.

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## INTERLAYER DIFFUSION IN LANGMUIR-BLODGETT MULTILAYERS CONTAINING LAYERS OF TWO TYPES

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 (Max Planck-Institute for Polymer Research, Mainz, Germany)  
 and  
 S. Satija and C. Majkrzak

Interdiffusion between layers of Langmuir-Blodgett (LB) multilayers has been studied very little, despite the fact that understanding this phenomenon is critical for the development of nanoscale devices exploiting the precise layer thickness and highly ordered structure attainable by LB deposition. This study compares interdiffusion in multilayers containing only a "classical" short chain amphiphilic molecule, Cadmium Arachidate (CdA) with that in a mixed multilayer including a bilayer of a rod-like polyglutamate copolymer with flexible aliphatic side chains, poly- $\gamma$ -methyl-L-glutamate-co- $\gamma$ -n-alkyl-L-glutamate (PG) [1]. Both neutron and x-ray reflectometry (NR & XR) are used as probes because the two techniques rely on different types of contrast in the system and thus provide complementary information.

Multilayers of CdA alone were studied first because their room temperature structure has been extensively characterized using a variety of techniques and some characterization data on their behavior at elevated temperature exists [2]. Our reflectometry measurements were intended

to reproduce and expand on the few qualitative NR measurements of interdiffusion at 70 °C by Stroeve et al. [3] and then become the basis for comparison measurements from a mixed multilayer containing both CdA and PG.

A multilayer containing six layers of protonated (p-) CdA followed by four layers of perdeuterated (d-) CdA were deposited on silicon substrates as shown in figure 1. Use of the deuterated species provided neutron contrast between the two packets of layers. X-ray reflectometry, which was sensitive to the position of the  $\text{Cd}^{++}$  ions attached to every molecule, but not to differences between d-CdA and p-CdA indicated that the definition of individual layers in an "as prepared" multilayer was good. NR measurements revealed, however, that some interchange of protonated and deuterated molecules between layers had already taken place even before annealing at elevated temperature, perhaps during deposition itself. While a very slight change in the NR curve from this sample occurred upon heating to 70 °C for 15 min, no further change was

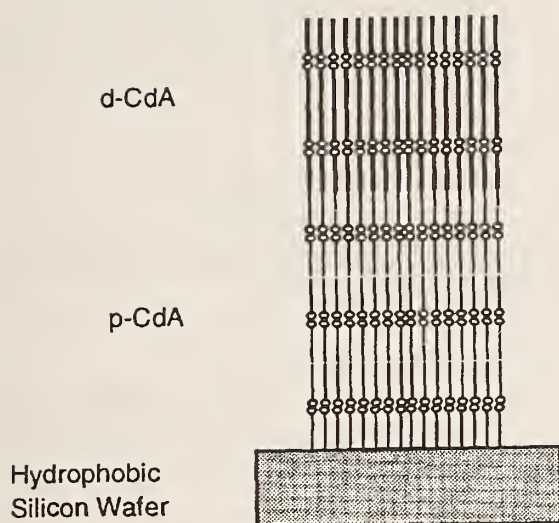


Figure 1. Schematic structure of the CdA multilayer for which the reflectivity is shown in figure 2.

observed after an additional 2.25 hr at 70 °C and 5.75 hr at 81 °C. A repetition of the x-ray measurement after the entire annealing regimen reproduced the curve seen before annealing, indicating no disordering of the layered structure had taken place. Our observation of little change with annealing at 70 °C contrasted sharply with the results of Stroeve et al., who reported significant change in the NR curve of a similar sample after annealing only 15 min at 70 °C<sup>3</sup>.

A second sample was chilled to 4 °C immediately after deposition and kept at 4 °C except during measurements and during annealing at 84 °C for various lengths of time. Reflectometry of the "as-deposited" sample again indicated some interdiffusion had already taken place before annealing. Further measurements, of which one is shown in figure 2, showed progressive, but subtle changes in the reflectivity after total annealing at 84 °C for 2, 10, and 33 hr.

A third system was made with a single PG bilayer sandwiched between six layers of p-CdA and six layers of d-CdA with the intent that the PG would act as a diffusion barrier. After annealing at 84 °C this sample's NR curve was changed significantly as shown in figure 3. Comparison with figure 2 reveals that, in fact, this change was greater than that for the

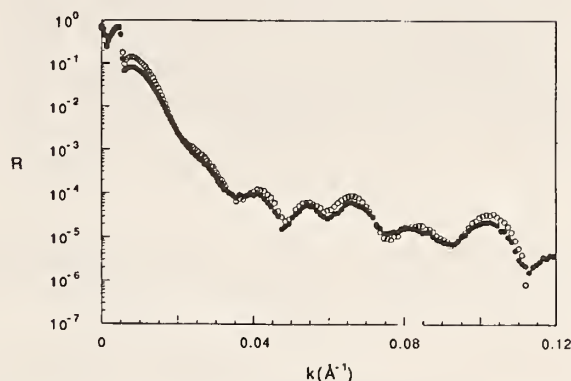


Figure 2. Comparison of the neutron reflectivity curves for the CdA multilayer as deposited (o) (kept at 4 °C until measurement) and annealed 10 hr at 84 °C (•).

multilayer without the PG bilayer annealed in the same way. Measurements at 70 °C revealed a similar trend. Modelling of the data is proceeding in order to quantify the degree of interdiffusion in each as-deposited sample and to identify the microstructural changes which occur during annealing.

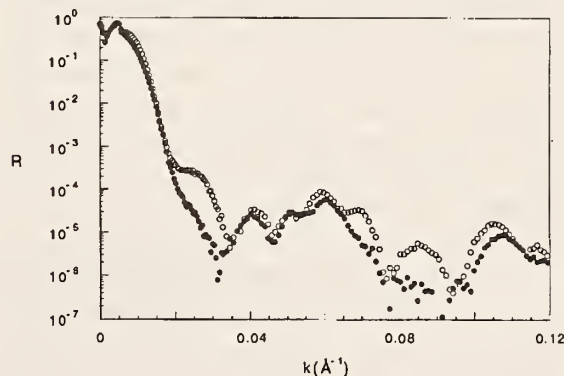


Figure 3. Neutron reflectivities of a multilayer consisting of six layers of p-CdA, a bilayer of PG, and six layers of d-CdA as deposited (o) and after annealing 10 hr at 84 °C (•).

Polyglutamates provided by K. Mathauer and Prof. G. Wegner, MPIP. Dr. W. Schrepp of BASF AG assisted in multilayer preparation. Research support provided by the Bundesministerium für Forschung und Technologie (BMFT) and the University of Akron.

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## MICROSTRUCTURE AND INTERLAYER DIFFUSION IN LANGMUIR-BLODGETT MULTILAYERS OF A ROD-LIKE COPOLYMER

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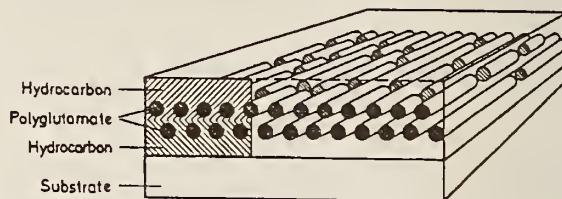
and

S. Satija and C. Majkrzak

The "as deposited" microstructure and interlayer diffusion in Langmuir-Blodgett (LB) multilayers of a rod-like polyglutamate copolymer with flexible aliphatic side chains, poly- $\gamma$ -methyl-L-glutamate-co- $\gamma$ -n-alkyl-L-glutamate [1] (PG) have been studied using neutron and x-ray reflectometry (NR & XR). Both protonated (p-) and deuterated (d-) species of PG were used to provide contrast between layers for NR. At the same time XR was insensitive to the distinction between protonated and deuterated layers, but was sensitive to the slight (ca. 5%) electron density difference between the PG backbone and side chains within a layer, thus providing a complementary sensitivity.

A model of the unannealed microstructure which described well both the reflectometry data collected in this study as well as earlier reflectometry data [2] and results from other techniques [1] is shown in figure 1. The PG molecules arranged themselves in bilayers with the rod-like, hydrophilic backbones localized at the center of the bilayer while the aliphatic, hydrophobic side chains segregated to the top and bottom of each bilayer.

Interdiffusion between and within bilayers was studied using three types of multilayers. The first was constructed to have contrast between adjacent bilayers and could be characterized by the layer sequence 'ppdd'. That is, the multilayer consisted of two protonated layers, comprising a single bilayer, followed by two deuterated layers, followed by two protonated layers, etc. A second sample, characterized by 'pdpd', allowed sensitivity to



**Figure 1.** Schematic of the PG bilayer structure, shown for the case of a single bilayer on a hydrophobic substrate.

interchange between any two layers, and a third sample, 'pddp', was designed to probe interchange between layers within a bilayer.

Neutron measurements from the ppdd and pdpd structures after annealing at 70 °C revealed no significant interchange between bilayers or between layers within a bilayer. Data from the pdpd structure is shown in figure 2. Likewise, neutron reflectometry of the pddp sample after annealing at 84 °C revealed no interchange, though the bilayer spacing did decrease slightly, suggesting a relaxation of the structure had occurred. X-ray reflectivity curves of all the as-deposited sample types exhibited a broad first order Bragg peak resulting from the spacing between backbones, as shown in figure 3. This peak's intensity was significantly weakened by annealing at either 70 or 84 °C, suggesting that a rearrangement of the backbones within the bilayer had occurred. Development of a detailed microstructural model which is consistent with the entire x-ray and neutron reflectivity curves before and after annealing will allow us to describe this rearrangement quantitatively.

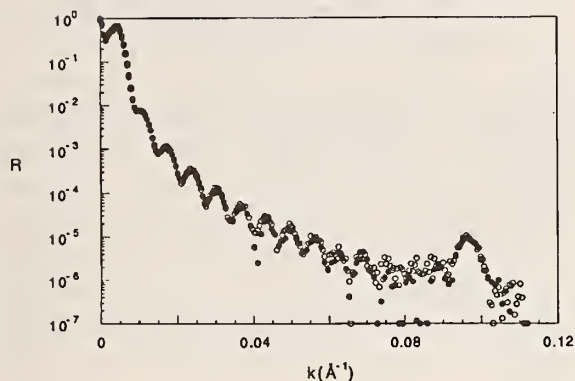


Figure 2. Neutron reflectivities of the 'pdpd' multilayer before annealing (o) and after (•) annealing 4 hr at 70 °C.

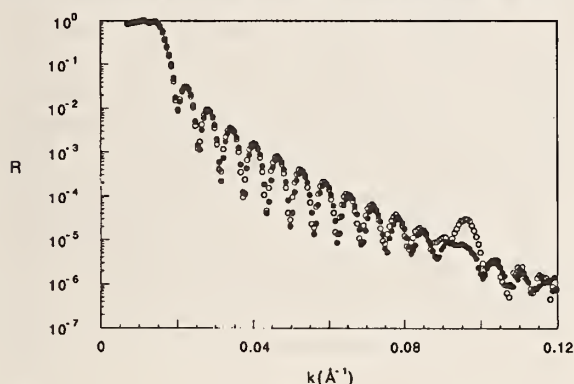


Figure 3. X-ray reflectivities of the 'pdpd' multilayer before annealing (o) and after (•) annealing 4 hr at 70 °C.

Polyglutamates provided by K. Mathauer and Prof. G. Wegner, MPIP. Dr. W. Schrepp of BASF AG assisted in multilayer preparation. Research support provided by the Bundesministerium für Forschung und Technologie (BMFT) and the University of Akron.

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## NEUTRON REFLECTIVITY STUDIES OF MITOCHONDRIAL OUTER MEMBRANES

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and

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Biological membranes are assemblies of lipid and protein molecules arranged as a continuous bilayer 4 to 5 nm thick [1]. Lipid molecules have hydrophobic (nonpolar) tails and a hydrophilic (polar) head group. When surrounded by water, the lipid molecules can form a bilayer, with the hydrophilic head groups facing outward toward the water and the hydrophobic head groups sandwiched between them. Thus, the membrane forms a 2-d solvent for membrane proteins, which are not water-soluble. A schematic representation of a section of cell membrane is shown in figure 1.

Some membrane proteins form hydrophilic transmembrane channels which allow molecules of the appropriate size and charge to pass through. Some of these channel proteins respond to an electrical potential, changing their conformation to allow the channel to open or close. In mitochondria, the outer membrane contains proteins that form large-diameter channels [2], VDAC (voltage-dependent anion-selective channels). These channels provide an opening for small molecules necessary for mitochondrial respiration and metabolism to pass through the outer membrane. At low potentials, the channel is in an "open" state. However,

when a potential is applied across the membrane, the channels close.

The neutron reflectivity technique [3] is being used to study the VDAC channels in the outer membrane of *Neurospora crassa* mitochondria. A single bilayer membrane will be measured in aqueous solvent at low potentials and at higher potentials. Changes in the neutron scattering length density profile perpendicular to the bilayer surface will be examined as a function of channel opening and closing. Since the lipid and the protein components of the membrane have different neutron scattering lengths, the contribution from one component can be enhanced by using a solvent containing an

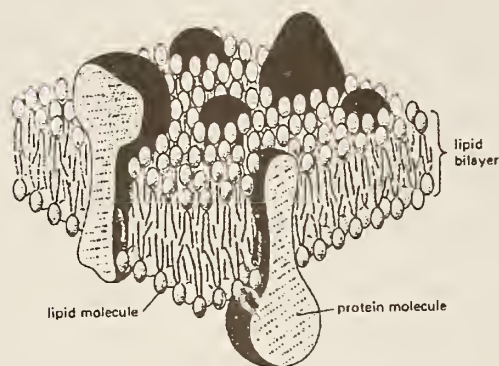


Figure 1. Schematic representation of a cell membrane (taken from ref. 1).

appropriate mixture of  $\text{H}_2\text{O}/\text{D}_2\text{O}$ . Experiments performed by two of the authors (D. Gurley and M. Colombini) indicate that the VDAC channels are functional in  $\text{D}_2\text{O}$  solvent.

It is important to make a sample consisting of a single, uniform lipid bilayer membrane. If multiple layers and/or nonuniform layers exist, a large percentage of the channel proteins may not be able to interact freely with the solvent. Therefore, changes in the membrane due to channel function may not occur in all layers, making them difficult to detect. Since the mitochondrial outer membranes must be isolated from *N. crassa*, they are only available in very small quantities. Therefore, a more readily-available soybean phospholipid (asolectin) is being used in initial experiments.

Control samples consisting of asolectin bilayers without the VDAC channel protein are being prepared on single-crystal silicon substrates containing a thin ( $\sim 1$  nm) oxide layer using a three-step technique. First, a monolayer is formed on the substrate by dipping it into a water trough with a monolayer spread on the water surface. A second monolayer is spread across the surface of water in a shallow well on a substrate backing. The substrate is then sandwiched on top of the backing to form the bilayer.

Neutron reflectivity profiles from the control samples will be fit to models for 4 to 5 nm uniform bilayers in order to check the integrity of the sample preparation method. If the asolectin samples prove to be uniform bilayers, mitochondrial outer membrane bilayers can be prepared in the same manner. The neutron reflectivity profile will then be measured for the outer membrane sample in an electrochemical cell as a function of applied voltage across the bilayer membrane.

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## C. MATERIALS SCIENCE

While much of the work performed at the NBSR could have been identified as Materials Science, we have chosen to include primarily those activities which are more traditionally included in this area in MSEL, such as studies of polymers and ceramics, residual stress, etc. A non-traditional area—neutron autoradiography of paintings—is also included here, reflecting the origins of the technique, as well as the breadth of the activities under way. Not all of the work performed is reflected in this report; for example, a SANS study of creep cavitation is not reported, even though it was almost completed by the time of the report. In assessing this program, it should be noted that the new 30-m SANS was just coming on line at the end of the period, and that the results of studies requiring the new capability will be more fully reflected in future reports.

SANS studies of polymers have always been a large part of the NIST program, reflecting the close interaction between the

Polymer Division and the Reactor Radiation Division. Once again, this program has been highly productive, and is clearly growing now that the 8-m SANS is devoted to Polymer Division work for 75% of available time. In addition, the burgeoning field of neutron reflectivity studies as a probe of surfaces and interfaces has a special role to play in polymer science, and that is reflected in this year's accomplishments.

Another area that is receiving renewed attention and focus is non-destructive residual stress and texture measurements, where additional staff and new instrument developments are aimed at an enhanced capability in this area. Efforts in this area include a program to study residual stress in the context of fatigue failure in axles, and a new program—under ONR sponsorship—to characterize residual stresses in weldments. Results in the new area are now being obtained, and will be reported next year.

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## SANS FROM PSD/PVME/PSH TERNARY POLYMER BLENDS

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and

R. Briber and B. Bauer (Polymers Division)

When used along with the Random Phase Approximation [1] (RPA), the Small-Angle Neutron Scattering (SANS) technique has proven to be most valuable for the determination of the Flory interaction parameter ( $\chi$ ) in binary polymer blends. Phase decomposition diagrams have been mapped out for a number of binary mixtures, such as the deuterated polystyrene (PSD)/poly(vinylmethyl ether) (PVME) system [2], through a determination of the spinodal line. Temperature and composition dependences of  $\chi_{\text{PSD/PVME}}$  have also been measured [2]. Following the recent extension of the RPA formalism to multicomponent systems [3,4], we have taken SANS data from a ternary polymer mixture of PSD, PVME and PSH ("hydrogenated" polystyrene). This system involves

three binary-interaction  $\chi$  parameters ( $\chi_{\text{PSD/PVME}}$ ,  $\chi_{\text{PSH/PVME}}$  and  $\chi_{\text{PSD/PSH}}$ ), two of which are fairly well known ( $\chi_{\text{PSD/PVME}}$ ,  $\chi_{\text{PSD/PSH}}$ ). The third one,  $\chi_{\text{PSH/PVME}}$ , is needed for the interpretation of light scattering data, whereby until now, one had to either approximate  $\chi_{\text{PSH/PVME}}$  by  $\chi_{\text{PSD/PVME}}$  and introduce uncertainties (20 °C shifts of the cloud point for deuterated and nondeuterated PS/PVME blends have been observed) or be compelled to use deuterated polystyrene even for photon scattering!

For an incompressible ternary mixture of homopolymers (A, B, C), the RPA gives for the partial structure factors:

$$S_{AA}(Q) = S_{AA}^0(1 + V_{BB}S_{BB}^0)/\Delta$$

$$S_{AB}(Q) = -S_{AA}^0V_{AB}S_{BB}^0/\Delta$$

where  $\Delta =$

$$(1 + V_{AA}S_{AA}^0)(1 + V_{BB}S_{BB}^0) - V_{AB}^2S_{AA}^0S_{BB}^0$$

and  $S_{AA}^0(Q) = N_A\phi_A v_A P_A(Q)$  is a bare

structure factor and  $N_A$ ,  $\phi_A$ ,  $v_A$ , and  $P_A(Q)$  are the degree of polymerization, volume fraction, monomeric volume, and Debye function, respectively. The third component enters only through:

$$V_{AA}(Q) = 1/S_{CC}^0(Q) - 2 X_{AC}/v_0$$

$$V_{AB}(Q) =$$

$$1/S_{CC}^0(Q) + X_{AB}/v_0 - X_{AC}/v_0 - X_{BC}/v_0.$$

The neutron scattering intensity is given by:

$$I(Q) = (\ell_A/v_A - \ell_C/v_C)^2 S_{AA}(Q) +$$

$$(\ell_B/v_B - \ell_C/v_C)^2 S_{BB}(Q) +$$

$$2(\ell_A/v_A - \ell_C/v_C)(\ell_B/v_B - \ell_C/v_C)S_{AB}(Q)$$

where the  $\ell$ 's are the monomeric scattering lengths for the different components.

A set of three PSD/PVME/PSH samples were prepared with weight average molecular weights of:  $1.95 \times 10^5$ ,  $1.59 \times 10^5$ , and  $1.90 \times 10^5$  g/mole, respectively with polymer compositions for which the PVME fraction was kept constant at 50% by weight. It is interesting to see that the reduced SANS data do not follow the intuitive trend that one expects based on previous binary blends experiment; i.e., the scattered intensity at low  $Q$  does not necessarily increase with temperature. In fact, the low  $Q$  intensity can even decrease with temperature (fig. 1) at first before increasing close to the spinodal temperature. This can be understood in the framework of the three component RPA as an interplay of the various terms in the scattering function.

Results of the fits showed that  $X_{PSH/PVME}$  has the following temperature dependence:

$$X_{PSH/PVME}/v_0 = 10.4 \times 10^{-4} - 0.43/T$$

( $T$  is in  $^{\circ}\text{K}$ ). The obtained  $X_{PSH/PVME}$  shows that the spinodal temperature for the PSH/PMVE system is  $20^{\circ}\text{C}$  lower than that of PSD/PVME in agreement with cloud point measurements. Figure 2 shows that the temperature variations of  $X_{PSD/PVME}$  and  $X_{PSH/PVME}$  are linear and parallel to each other which means that deuteration brings about a uniform shift in temperature of about  $20^{\circ}\text{C}$ .

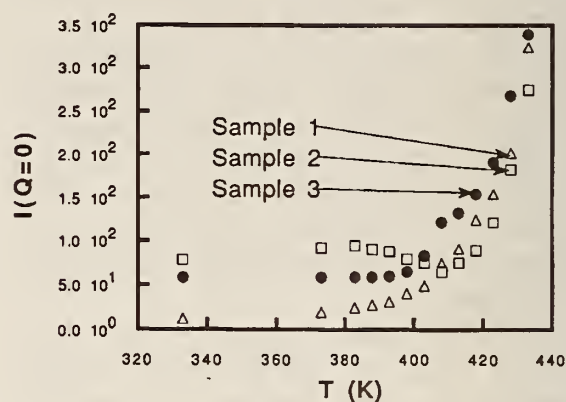


Figure 1. Low  $Q$  intensity  $I(Q = 0.085 \text{ nm}^{-1})$  for samples 1, 2 and 3 with increasing temperature.

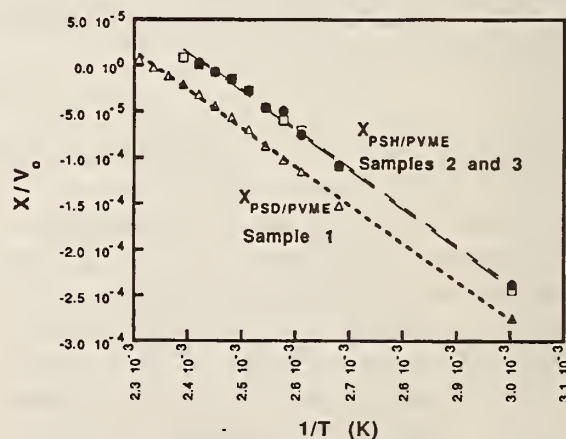


Figure 2. Variations of  $X_{PSD/PVME}$  (obtained from sample 1) and  $X_{PSH/PVME}$  (obtained from samples 2 and 3).

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## SMALL ANGLE NEUTRON SCATTERING FROM DEUTERATED POLYSTYRENE IN DIOCTYL PHTHALATE SOLUTION UNDER SHEAR

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and

A. I. Nakatani, D. Waldow, and C. C. Han (Polymers Division)

High molecular weight polystyrene is known to incur a shear induced phase separation in dilute solution [1]. Small angle neutron scattering (SANS) has been applied in order to investigate the thermodynamics of high molecular weight ( $1.95 \times 10^6$  g/mole) deuterated polystyrene (PSD) in dioctyl phthalate (DOP) solution at around 3% concentration and under steady shear. SANS measurements were made on the new NIST/EXXON/UofMN 30 m instrument at many shear rates ranging from the quiescent state ( $0 \text{ s}^{-1}$ ) to  $1100 \text{ s}^{-1}$ . SANS data were corrected for empty cell and beam blocked background scattering. Scattering from pure DOP solvent was also rescaled and subtracted. As evidenced from isointensity contour maps (fig. 1) and from sector averaging of the data in horizontal and vertical directions, the scattering was isotropic (even for the highest shear rates) so that circular averaging was justified. Figure 2 shows the corrected data for a few runs.

The Random Phase Approximation (RPA) was used to describe [2] the corrected and reduced SANS data. Fits were made to the form:

$$(b_p/v_p - b_s/v_s)^2/I(Q) = \\ 1/N_p v_p \phi_p D(Q) + 1/v_s \phi_s - 2X_{ps}/v_o$$

where the usual notation has been used for the polymer (solvent) scattering length  $b_p$  ( $b_s$ ), monomer volume  $v_p$  ( $v_s$ ), volume fraction  $\phi_p$  ( $\phi_s$ ), degree of polymerization  $N_p$ , interaction parameter  $X_{ps}$  and swollen Debye function  $D(Q)$ :

$$D(Q) = 2 [\exp(-U) - 1 + U]/U^2;$$

$$U = Q^2 b^2 N^{2v} / (2v + 1)(2v + 2)$$

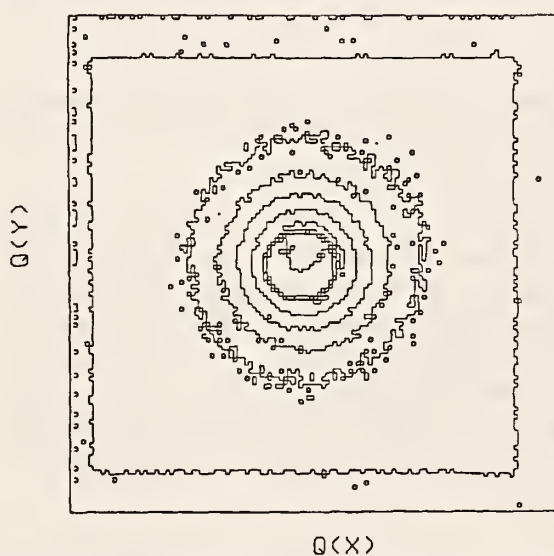


Figure 1. Isointensity contour maps of the SANS intensity for a shear rate of  $323.32 \text{ s}^{-1}$ .

and  $v$  is the excluded volume parameter ( $v = 0.6$  was used here). Results of the fits are reasonable and the extracted interaction parameter  $X_{ps}$  was found to increase with shear rate as expected (fig. 3). Beyond a predicted spinodal value  $X_{ps}^s$ , the RPA model breaks down and the extracted  $X_{ps}$  parameters are not to be trusted any longer. It is interesting to note that  $I(0)$  and  $X_{ps}$  show a steep variation beyond a "critical" shear rate (around  $S_c = 57 \text{ s}^{-1}$ ) which is still below the shear rate corresponding to the "apparent" spinodal point ( $S_s = 280 \text{ s}^{-1}$ ).

This use of the RPA is equivalent to assuming that shear affects the monomer/solvent interaction ( $X$ ) parameter only. This may be

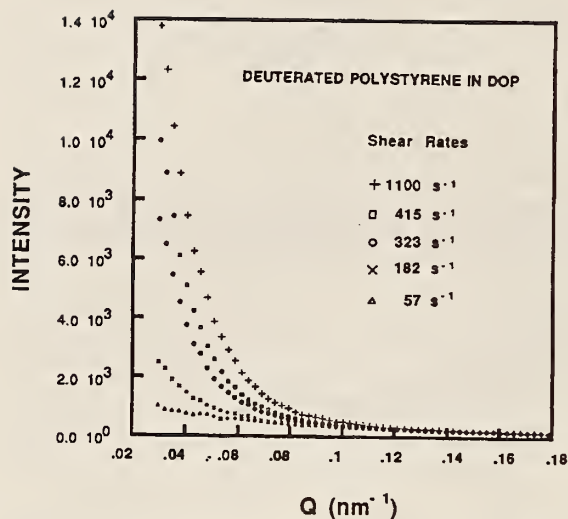


Figure 2. Corrected and reduced SANS data from PSD in DOP solution for some of the measured shear rates. The intensity is in an arbitrary scale.

unrealistic and effects may exist on conformations (entropic term in the Flory-Huggins equation) through hydrodynamic interactions. Based on common sense, one would expect shearing (i.e., a form of shaking) to induce remixing (as observed for polymer blends). High molecular weight polystyrene solutions, however, points to the contrary,

showing shear-induced phase separation which has to be driven by either a reduction of the entropic term or an increase of the enthalpic term in the Flory-Huggins equation. Different approaches based on solutions of the hydrodynamic equations with a shear term included would be a more appropriate description.

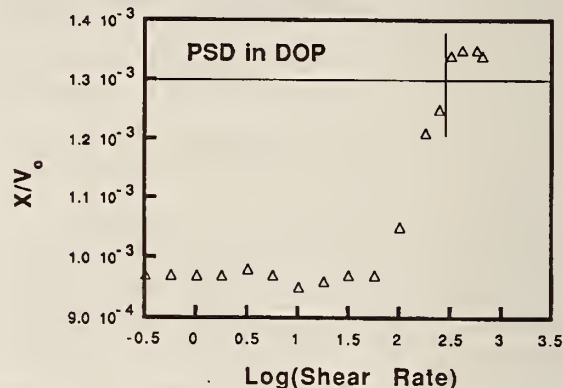


Figure 3. Variation of the extracted polymer-solvent interaction parameter  $X_{ps}$  with shear rate. The horizontal line corresponds to the predicted "apparent" spinodal line.

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## STRUCTURE FACTOR FOR "DENDRIMER" POLYMER GELS

B. Hammouda

Advances in polymer synthesis are making possible the polymerization of complicated chain architectures. Synthesis of highly regular structures such as "stars", "combs", "dendrimers", etc have now been achieved. "Dendrimers" [1,2] are regular polymer gels that grow through multifunctional polymerization starting from a central core and branching outward with a multiplication of the number of monomeric blocks from one generation to another. Advances in the interpretation of small-angle neutron scattering data, based on the random phase approximation model, on the other hand, have made possible the characterization of rather complicated polymer systems provided that the "bare" (single-chain) structure factors

are available. In anticipation of the performance of SANS measurements on dendrimer gels in solution or mixed with other compatible polymers, the single-chain structure factor for such a gel has recently been calculated.

The calculation of the various terms involved are straightforward. There are four main contributions to the correlations: (1) one intra-branch self-correlations part,  $S_{sb}^s$ , (2) one intra-branch cross-correlations part between blocks that originate from the same stem,  $S_{sb}^f$ , (3) one intra-branch cross-correlations part between blocks that originate from different stems,  $S_{sb}^a$ , and (4) one inter-branch correlations part  $S_{ib}$ . The results are:

$$S_{sb}^s(Q) = [(f^N - 1)/(f - 1)] P(a, n).$$

$$S_{sb}^f(Q) = 2 \{ [F(a, n)]^2 / [f \exp(-an) - 1] \} \\ \{ f^N \exp(anN) [\exp(anN) \exp(an)] / [\exp(an) - 1] \\ - f(f^N - 1)/(f - 1) \}$$

$$S_{sb}^a(Q) = 2 [F(a, n)]^2 \{ (f - 1) / [f \exp(-2an) - 1] \} \\ \{ A(Q) + B(Q) \}$$

$$A(Q) = [f^{2N} \exp(-2anN) \\ - f^2 \exp(-2an)] / [f^2 \exp(-2an) - 1] - (f^N - f)/(f - 1)$$

$$B(Q) = 2 \{ f^N \exp(-anN) [f^N \exp(-anN) \\ - f \exp(-an)] / [f \exp(-an) - 1] \\ - f \exp(-an) [f^2 \exp(-2anN) \\ - f^2 \exp(-2an)] / [f^2 \exp(-2an) - 1] \\ - f^N \exp(-anN) [\exp(anN) - \exp(an)] / \\ [\exp(an) - 1] + f \exp(-an) (f^N - f)/(f - 1) \} / \\ [f \exp(-an) - 1]$$

$$S_{ib}(Q) = \\ [F(a, n)]^2 [f^N \exp(-anN) - 1]^2 / [f \exp(-an) - 1]^2.$$

The total structure factor is the sum of all of these partial structure factors:

$$S(Q) = N_b [S_{sb}^s(Q) + S_{sb}^f(Q) + S_{sb}^a(Q)] \\ + N_b(N_b - 1) S_{ib}(Q).$$

In order to normalize  $S(Q)$  to unity, one has to divide it by the square of the total number of monomers in the gel:  $[nN_b(f^N - 1)/(f - 1)]^2$ .

The following parameters have been used:  $N_b$  is the number of branches in the dendrimer,  $N$  is the number of generations of monomeric blocks,  $f$  is the multiplication factor between two subsequent generations,  $n$  is the number of monomers in each block forming Gaussian links of segment length  $b$ . Moreover  $F(a, n)$  and  $P(a, n)$  are the form and structure factors respectively for finite chain portions of length  $n$ :

$$F[a, n] = [1 - \exp(-an)]/a.$$

$P[a, n] = n + 2n^2 \{ 1 - [1 - \exp(-an)]/na \} / (an)^2$  and  $a = Q^2 b^2 / 6$  is a dimensionless scattering variable.

#### DENDRIMER POLYMER GEL

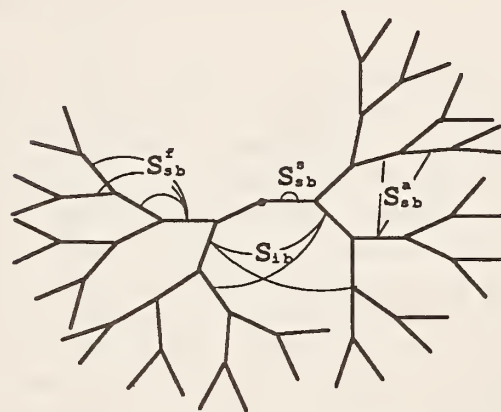


Figure 1. Schematic 2-d representation of a dendrimer polymer gel.

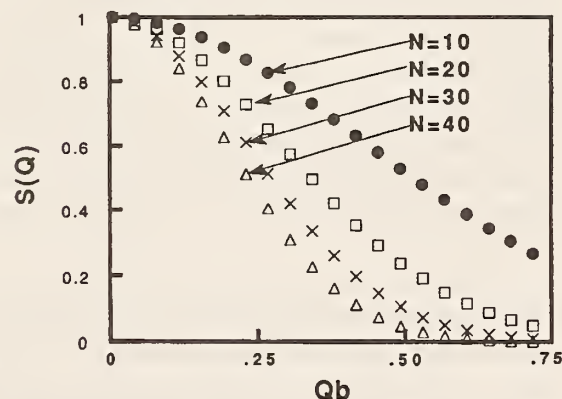


Figure 2. Variation of the structure factor  $S(Q)$  with the dimensionless variable  $Qb$  for a dendrimer polymer gel with  $N_b = 3$ ,  $f = 2$ ,  $n = 1$ , and with  $N$  varying from 10 to 40.

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QUASIELASTIC NEUTRON SCATTERING STUDY OF THE DYNAMICS  
OF WATER IN CURING CEMENT

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Concrete is one of the world's most important materials, yet its fundamental chemistry is not completely understood. It is known that the cement gains its strength through the reaction of the starting materials with water. During the curing process, which takes several months to complete, several hydrated compounds form and then further react with each other. These phases have been difficult to measure because they tend to be poorly crystallized colloids or fibers. The physical state of water in the material is a critical factor defining the progress of the reactions, but in the past this could only be measured indirectly through drying experiments. The lack of direct information on the state of the water has led to a number of conflicting models of the cement microstructure based on differing concepts of water bound in the crystal structure as hydroxyl groups ( $\text{OH}^-$ ) or interlayer water molecules, free water, and water adsorbed on surfaces or in various sizes of pores [1].

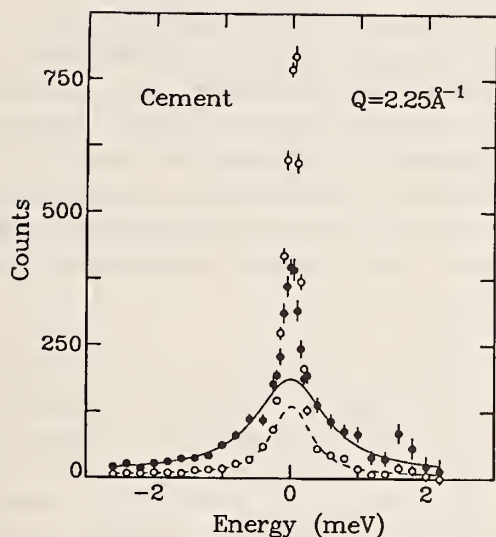
To resolve this issue and to get a clearer picture of the kinetics of the cement reactions, we have undertaken a time-resolved quasielastic neutron scattering study of the process. This method is especially suitable because neutron scattering is very sensitive to hydrogen and because energy gained or lost in the scattering process is a direct measure of the dynamic state of the water molecules.

The preliminary data reported here were obtained using the BT-2 triple axis spectrometer with a fixed initial energy of 4.85 meV and collimations of 60'-40'-40'-80' before and after the pyrolytic graphite monochromator and analyzer crystals, respectively. This configuration yields an energy resolution of 0.22 meV at the elastic position. The measured background was subtracted and a correction was

applied to account for the changing resolution volume of the secondary spectrometer.

Figure 1 shows two quasielastic spectra for cement. The closed circles are data obtained immediately after mixing the cement, whereas the open circles are data taken 16 days later. These spectra were fit to a  $\delta$ -function plus a Lorentzian, convoluted with a Gaussian resolution function. The Lorentzian component of these fits is displayed as a solid line for data taken immediately after mixing the cement and as a dashed line for the data taken 16 days later. Two effects are readily apparent. The first is that the integrated intensity of the Lorentzian with respect to the elastic component has decreased markedly with time indicating that much of the water has become immobile on the time scale of these measurements. In addition, the width of the Lorentzian has decreased by about a factor of 2, leading to the conclusion that the portion of the water which is still mobile, is not moving as rapidly as it was originally.

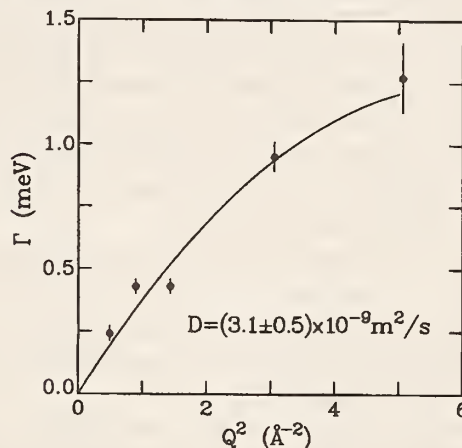
In order to gain information on the type of motion involved, measurements of the Q-dependence of the width of the Lorentzian component immediately after mixing have been made (fig. 2). Here the solid line is a fit to a parabola which is a low Q approximation to the scattering function expected for translational diffusion. This procedure yields a diffusion constant of  $(3.1 \pm 0.5) \times 10^{-9} \text{ m}^2/\text{s}$ . This is very similar to that obtained by Teixeira et al. [2] for bulk water. Thus these preliminary results show that when originally mixed, the water in cement behaves essentially like bulk water. However, the amount of mobile water decreases with time and the speed with which it diffuses also decreases.



**Figure 1.** Quasielastic neutron scattering spectra for cement at  $Q=2.25 \text{ \AA}^{-1}$ . The closed circles are data taken immediately upon mixing the cement, while the open circles represent data taken 16 days later. The solid and dashed line represent the fitted Lorentzian component of this data.

Quasielastic neutron scattering thus gives a direct characterization of the state of the water in cement during the curing process. This provides a powerful analytical tool that can be used to study many aspects of cement chemistry. These include the effects of environmental conditions such as temperature on the ultimate strength of the material, a critical factor in the safe

construction of structures. Also, the effects of additives such as fly ash or silica fume on the cement curing process can be studied. This kind of knowledge will be directly applicable to the restoration of the national infrastructure.



**Figure 2.** The width of the quasielastic component as a function of  $Q^2$  obtained immediately after mixing. This data is indicative of translational diffusion and is consistent with the results obtained for bulk water [1].

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## SMALL ANGLE NEUTRON SCATTERING STUDY OF THE MISCIBILITY OF SBR/PB BLENDS

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and  
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Miscibility of different kinds of rubber is an interesting and important problem for rubber industry. Miscible blends are favored in some cases, but phase-separated blends with well-controlled domain size which could improve physical properties are favored in other cases. The progress of technology made it possible to synthesize tailor-made polymers with a pre-determined molecular weight, microstructures and copolymer composition. If one can predict the miscibility of the blend with given molecular

weights, microstructure and copolymer compositions of the constituent polymers, it will be a great advance in designing rubber/rubber blends with the desired properties.

Because of the plural microstructures formed in the polymerization reaction, most of the synthetic polydienes are copolymers made of only one kind of monomer. Therefore, the blends of polydienes should be considered as blends of copolymers. In our previous paper [1], we have reported the small-angle neutron

scattering (SANS) analysis to determine the interaction parameters between various comonomers and to predict phase behavior for binary copolymer blends. We have also shown that the theory of random copolymer mixtures developed by ten Brinke et al. [2] works well for the blend systems of protonated polybutadiene (HPB) and perdeuterated polybutadiene (DPB), and protonated polyisoprene and DPB with various microstructure, and predicts successfully the miscibility of the binary blends of polydienes with different microstructure.

In this study [3] the miscibility of binary blends of deuterated polybutadiene (DPB) and poly(styrene-*r*-butadiene) (SBR) was measured by the small angle neutron scattering experiment and the interaction parameter,  $\chi_{\text{blend}}$ , was obtained. Using the copolymer theory, the fundamental segmental interaction parameters between the 1,2-butadiene (v) and the 1,4-butadiene (B),  $\chi_{vB}$ ; the 1,2-butadiene (v) and the styrene (s),  $\chi_{vs}$ ; and the 1,4-butadiene (B) and the styrene (S),  $\chi_{BS}$  were determined from the measured  $\chi_{\text{blend}}$ 's.

Using these interaction parameters,  $\chi_{vs}$ ,  $\chi_{BS}$  and  $\chi_{vB}$ , the miscibility of SBR/PB blends as a function of random copolymer composition, microstructure composition, blends composition, and molecular weights can be predicted. The predictions of the miscibility for several SBR/PB blends agreed very well with their phase diagram obtained by light scattering experiments.

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## THERMODYNAMICS OF HYDROCARBON POLYMER BLENDS BY SANS

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The goal of this effort is to understand the interaction between chemically distinct, saturated hydrocarbon polymers. In this report, we focus on the interactions between tetramethylene (TM) and ethylethylene (EE) units. We study these interactions by conducting small angle neutron scattering experiments on blends of random copolymers with varying amounts of EE units.

The polymer studies are referred to as  $hE_a(97)$ ,  $hE_b(97)$ ,  $hE(88)$ ,  $hE(78)$ ,  $dE_a(97)$ ,  $dE_b(97)$ ,  $dE(88)$  and  $dE(78)$ . The number in brackets refers to the mole % of EE units in each polymer. The prefix h implies that the polymer is fully hydrogenated while the prefix d implies that it is partially deuterated. The weight average degree of polymerization, N, based on

a  $C_4$  monomer unit, for each the polymers are given below. All polymers are nearly monodisperse with measured polydispersities of less than 1.06.

<u>Polymer</u>	<u>N</u>
$hE_a(97)$ , $dE_a(97)$	1643
$hE_b(97)$ , $dE_b(97)$	857
$hE(88)$ , $dE(88)$	1625
$hE(78)$ , $dE(78)$	1304

Blends of these materials were studied by light as well as neutron scattering. The scattering contrast between the polymer species in the blends derives primarily from differences in their deuterium contents. The critical point (single phase to two phase transition) for blends of hE(78)/dE(88) (volume fraction,  $v$ , of hE(78) was 0.5) was determined on a home-built light-scattering instrument that detects changes in total scattered intensity in the angular range between  $4^\circ$  and  $22^\circ$ . The sample was heated well above its estimated critical point for several days and then cooled in steps ranging between  $5^\circ\text{C}$  and  $50^\circ\text{C}$ . The onset of a phase transition was inferred from an increase in the measured scattered intensity with decreasing temperature. Data obtained from the hE(78)/dE(88) is given in figure 1. Based on these measurements, the critical temperature,  $T_c$ , for this mixture was found to be  $133 \pm 3^\circ\text{C}$ .

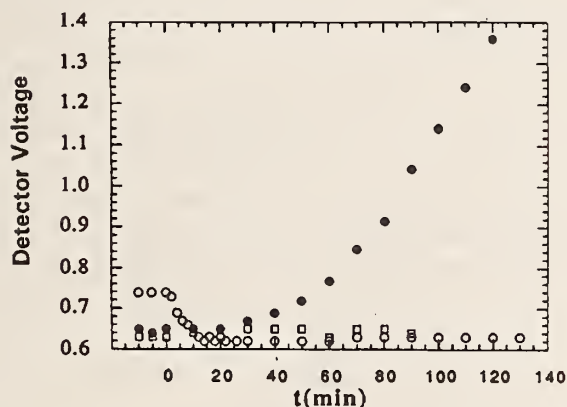


Figure 1. Light scattering results for hE(78)/dE(88) mixture (volume fraction of hE = 0.5) as it is quenched. The initial and final temperatures, respectively, for each data set are given below:  $180^\circ\text{C}$  to  $145^\circ\text{C}$  •  $145^\circ\text{C}$  to  $135^\circ\text{C}$  •  $135^\circ\text{C}$  to  $130^\circ\text{C}$ .

The temperature dependence of the Flory-Huggins  $\chi$  parameter, as measured by small angle neutron scattering for mixtures of 97% EE and 88% EE units (E(97) and E(88)) is given in figure 3. According to the Flory-Huggins theory, the  $\chi$  parameter represents the enthalpic interactions between monomer units and thus should be independent of molecular weight of the polymers and blend composition. The two blends considered here closely follow this

stipulation. Furthermore, the critical point estimated from the neutron scattering experiments on E(78)/E(88) mixtures are in agreement with the light scattering data.

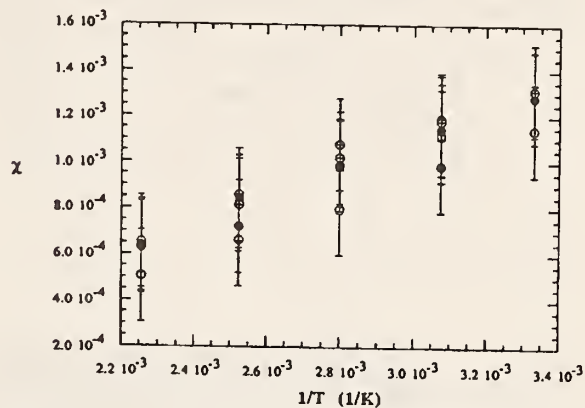


Figure 2.  $\chi$  versus  $1/T$  for E(97)/E(88) blends.  $\circ$  hE<sub>b</sub>(97)/dE(88) ( $\phi=0.50$ ).  $\oplus$  hE(88)/dE<sub>a</sub>(97) ( $\phi=0.50$ ).  $\square$  hE<sub>a</sub>(97)/dE(88) ( $\phi=0.05$ ).  $\bullet$  hE<sub>a</sub>(97)/dE(88) ( $\phi=0.75$ ). ( $\phi$  is the volume fraction of the hydrogenerated polymer).

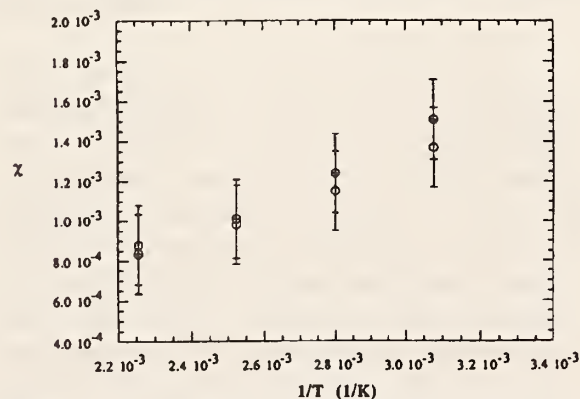


Figure 3.  $\chi$  versus  $1/T$  for E(97)/E(88) blends.  $\square$  hE(78)/dE(88) ( $\phi=0.50$ ).  $\oplus$  hE(88)/dE(78) ( $\phi=0.25$ ).  $\circ$  hE(88)/dE(78) ( $\phi=0.75$ ). ( $\phi$  is the volume fraction of the hydrogenerated polymer).

We have demonstrated that small angle neutron scattering can be used to determine the interactions between hydrocarbon polymer blends. Using this data, we can predict the thermodynamic properties of these blends. Since the measured  $\chi$  parameter was independent of molecular weight and composition we can generate phase diagrams for such TM-EE copolymer mixtures. One such phase diagram for a E(97)/E(88) blend with  $N = 1625$  (molecular weights - 90,000) is shown in figure 4.

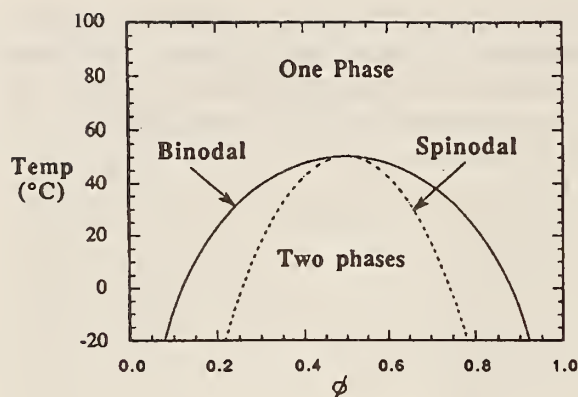


Figure 4. Predicted phase diagram for E(97)/E(88) blend (molecular weight of the two polymers = 90,000). ( $\phi$  is the volume fraction of E(97)).

### PHASE SEPARATION IN DEUTERATED POLY(CARBONATE)/ PROTONATED POLY(METHYLMETHACRYLATE) BLENDS NEAR GLASS TRANSITION TEMPERATURE

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and  
C. C. Han (Polymers Division)

Poly(carbonate) (PC) has been used extensively in the area of high performance engineering blends and alloys. Because of the relatively high glass transition temperature of PC, ( $T_g \approx 150^\circ\text{C}$ ) the available temperature range where experiments are normally performed to study the phase behavior (above  $T_g$ ) of a polymer blend is limited. There has been controversial reports about the miscibility of poly(carbonate) with other polymers especially with poly(methylmethacrylate).

In this study, deuterated poly(carbonate) (dPC) with  $M_w = 28 \times 10^3$  and poly(methylmethacrylate) (PMMA) with  $M_w = 33 \times 10^3$  are used. Samples with compositions of dPC/PMMA at 50/50, 40/60, and 30/70 have been prepared by fast solvent casting of thin films. This procedure allows us to freeze in the miscible distribution of the binary polymer mixtures into its glassy states. The time resolved small angle neutron scattering experiments are then performed after the temperature of a specimen is jumped from room temperature which is below its  $T_g$  to various temperatures above its  $T_g$ . In figure 1, the time evolution of scattering intensities,  $S(q,t)$ , of a 50/50 dPC/PMMA blend are displayed following

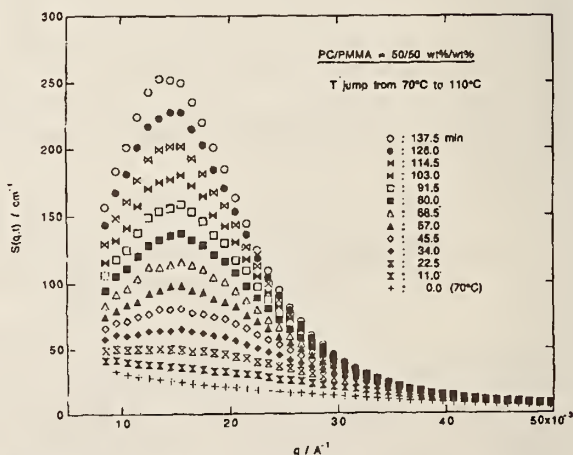


Figure 1. The time evolution of scattering intensities,  $S(q,t)$ , in the early stage of spinodal decomposition of a 50/50 dPC/PMMA blend following a temperature jump from  $70^\circ\text{C}$  to  $110^\circ\text{C}$ .

a temperature jump from  $70^\circ\text{C}$  to  $110^\circ\text{C}$ . It is clear that spinodal decomposition kinetics at the very early stage can be studied. By using the Cahn-Hilliard-Cook theory and following the procedure [1] we have developed earlier, the "virtual structure factor",  $S(q,\infty)$ , which is an analytical extrapolation of the static structure factor into the unstable two phase region, can be obtained in this experiment. In figure 2 the

virtual structure factor,  $S(q, \infty)$ , for the dPC/PMMA 50/50 blend at 110 °C obtained from the kinetics experiment is displayed as a function of  $q$ . The Ornstein-Zernike plot of this virtual structure factor which is  $S^{-1}(q, \infty)$  vs.  $q^2$  is shown in figure 3. The  $q_c$  which is the wavelength separating concentration fluctuation growth from decay in this spinodal decomposition kinetics is also indicated in the figure. The negative intercept which is related to  $\chi_s - \chi$  with  $\chi$  as the binary interaction parameter for the blends and  $\chi_s$  as the  $\chi$  at spinodal point provides a measure of the  $\chi$  parameter at 110 °C which is in the phase separated region and not accessible by any conventional measurement we know of.

In this study, we were able 1) to study the very early stage of spinodal decomposition starting from the dimension of the molecular size of a single polymer chain; 2) to confirm the Cahn-Hilliard-Cook theory in quantitative details; 3) to study the influence of the magnitude of the concentration fluctuation on the spinodal decomposition kinetics; 4) to obtain binary interaction parameters as a function of temperature in the unstable two phase region and then to calculate the free energy of mixing; 5) and to study the detailed spinodal decomposition kinetics in the intermediate and late stages which will be discussed separately.

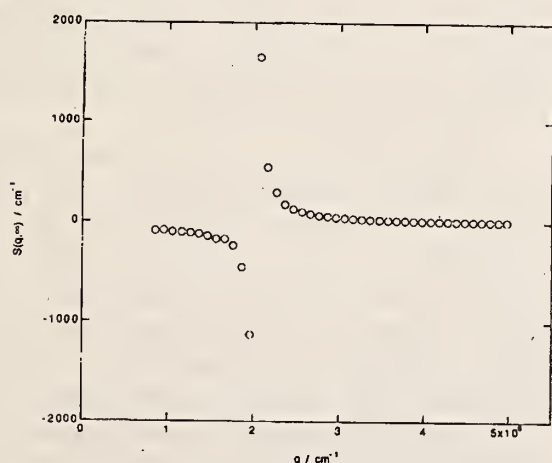


Figure 2. The "virtual structure" factor,  $S(q, \infty)$ , for the dPC/PMMA 50/50 blend at 110 °C obtained from the kinetics experiment is displayed.

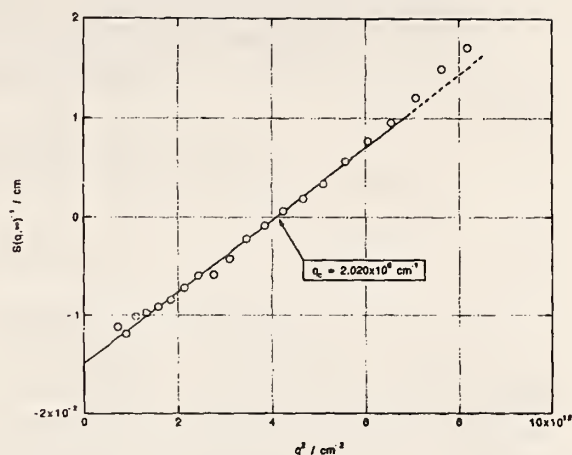


Figure 3. The Ornstein-Zernike plot of the above virtual structure factor is displayed. The critical wavelength,  $q_c$ , which separate the concentration fluctuation growth from decay is indicated.

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# NEUTRON REFLECTIVITY STUDY OF FINITE THICKNESS EFFECTS IN THE THERMODYNAMICS OF WEAKLY SEGREGATING DIBLOCK COPOLYMER THIN FILMS

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and

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Diblock copolymers can order and disorder on a microscopic scale with the variation of temperature or chain length,  $N$ . The entropic and enthalpic effects which control this transition are small in a weakly segregating system and therefore the presence of a thin film's symmetry breaking interfaces is expected to have a significant effect on the transition character and diblock microstructure. The microstructure of thin ( $1000 \text{ \AA} - 4000 \text{ \AA}$ ) films of a nearly symmetric ( $f = .55$ ) model diblock copolymer, poly(ethylenepropylene) - poly(ethylethylene) (PEP-PEE) spun cast on silicon substrates was studied using the neutron reflectometer on BT-7. Room temperature samples of several molecular weights bracketing that at which the bulk disorders were considered first. Then, the microstructures of films of a single molecular weight, but varying thickness were probed in a temperature range about the corresponding bulk order-disorder transition (ODT) temperature ( $125^\circ\text{C}$ ) [1]. The system studied here differed from the only other thin film diblock system studied to date [2], poly(styrene)-poly(methylmethacrylate) (PS-PMMA), in three ways: PEP-PEE was much less strongly segregating than PS-PMMA, neither PEP or PEE had specific attractions to the substrate and the difference between surface energies of the two blocks in the copolymer was less for PEP-PEE.

A primary result of the study is the finding that the PEE block locates preferentially at both interfaces for all samples types, regardless of chain length, deuterium labelling and film thickness. This is in stark contrast to PS-PMMA on silicon in which the composition at the polymer/substrate interface is almost pure PMMA, while the composition at the polymer/air interface is enriched in PS. The reason for

the symmetric structure of the PEP-PEE film is not yet understood.

A second important result of the work is the observation of a change in the temperature dependence of the microstructure with film thickness. For a relatively thick film ( $t \text{ ca. } 3900 \text{ \AA}$ ) of PEP-PEE having chain length,  $N$ , equal to 1026, the microstructure remains ordered throughout the film above the bulk ODT temperature of  $125^\circ\text{C}$ . A reasonably abrupt change in the character of the reflectivity curve at about  $135^\circ\text{C}$  signals a disordering of the film's "interior", while the microstructure near the two interfaces continues to be symmetrically ordered even to  $175^\circ\text{C}$  as shown in figure 1. The effect of the interfaces is thus not only to induce interfacial ordering, but also to shift the ODT temperature of the film interior up some  $10^\circ\text{C}$ . This shift is consistent with the notion that the presence of the interfaces is dampening composition fluctuations in the diblock causing it to disorder at higher temperature. Reducing the thickness of the film further to three times the bulk domain spacing leads to other qualitative changes in the disordering behavior which are still under study.

Disordering of the film with decreasing chain length at constant temperature was also observed. The range of chain lengths studied ( $N = 210$  to  $1890$ ) covered a variety of microstructures from nearly homogeneous to strongly segregated and demonstrated that surface ordering also persisted when the film disordering was caused by decreasing  $N$ . Composition profiles for four chain lengths at  $23 \pm 1^\circ\text{C}$  are shown in figure 2. Broadening of the domain interfaces with decreasing  $N$  can be clearly seen. Particularly interesting is the microstructure of the  $N = 790$  material, which is known to disorder at  $16^\circ\text{C}$  in the bulk.

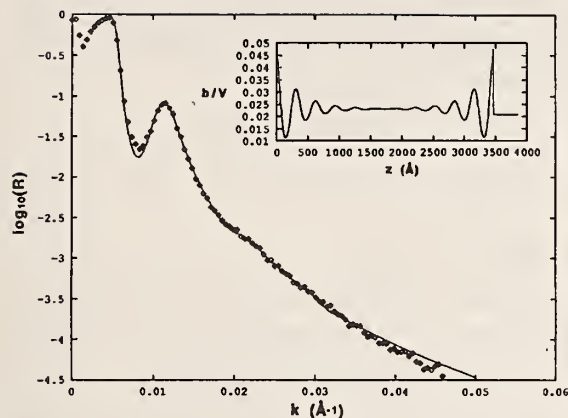


Figure 1. Experimental reflectivity curve (o) for thickest diblock film at 175 °C compared with the simulated reflectivity curve (solid line) for the model structure shown in the inset.

### MICROSTRUCTURE CHANGE WITH DECREASING N

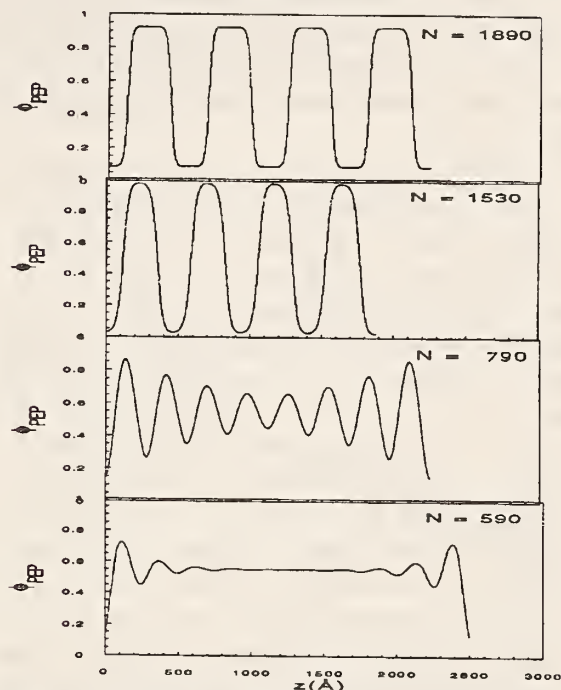


Figure 2. Variation of the thin film microstructure with decreasing N.

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## ORDER/DISORDER IN THIN DIBLOCK COPOLYMER FILMS

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The preferential interaction of specific block of symmetric diblock copolymers with the air and substrate interfaces has been shown to induce an orientation of the lamellar microdomain morphology parallel to the film surface for temperatures below the order-disorder transition temperature,  $T_{MST}$ . At higher temperatures, where the copolymer in the bulk disordered, the preferential interactions induce an oscillatory variation in the composition which decays with a characteristic length,  $\xi$ , as a

function of distance from the surface. These results, far from  $T_{MST}$ , were in quantitative agreement with mean field predictions [3]. In this study the influence of temperature and film thickness on the ordering symmetric diblock copolymers was investigated by neutron reflectivity.

Symmetric diblock copolymers of polystyrene, PS, and perdeuterated polymethylmethacrylate, d-PMMA, denoted P(S-b-d-MMA), were spin coated onto Si substrates from toluene

solutions. The thickness of the films was varied by varying the concentration of the copolymer. The specimens were annealed at the desired temperature and quenched to room temperature where the reflectivity measurements were performed. The experiments were performed on BT-7 at NIST.

Shown in figure 1 are a series of neutron reflectivity profiles for a 1.6  $\mu\text{m}$  thick film of P(S-b-d-MMA) as a function of temperature. The annealing temperature decreases as one proceeds from the bottom to top profile. It should be noted that experiments were performed with increasing and decreasing annealing temperatures to ensure reproducibility of the results. At high temperatures the reflectivity profile is characterized by a weak maximum occurring near  $k_{z,0} \sim 0.02 \text{ \AA}^{-1}$ . Very diffuse interference are seen at higher  $k_{z,0}$ . Such profiles are characteristic of copolymers in the disordered state where the concentration profiles from the air and substrate interfaces are given by an exponentially damped cosine function. As the temperature is decreased, the first reflection becomes sharper and more intense and the interferences at higher  $k_{z,0}$  become more pronounced. By modeling the reflectivity profiles it has been found that as one approaches  $T_{\text{MST}}$ ,  $\xi$  is nearly three times larger than that predicted from mean field arguments. Also,  $1/\xi^2$  varies as  $(1/T_{\text{MST}} - 1/T)$ , so that by extrapolation  $T_{\text{MST}}$  for the films can be determined. Decreasing the temperature further, marked changes in the reflectivity profile occur. Not only does the first order reflection appear but second and third order reflections at higher  $k_{z,0}$  become sharp and distinct. Such profiles are typical for a fully ordered P(S-b-d-MMA) morphology where the lamellar microdomains are oriented parallel to the film surface.

The values of  $T_{\text{MST}}$  are shown in figure 2 as a function of the film thickness. For thick specimens  $T_{\text{MST}}$  approaches the bulk value of 157  $^{\circ}\text{C}$ . However, as the film thickness is decreased, the temperature at which  $T_{\text{MST}}$  occurs increases dramatically. In fact,  $T_{\text{MST}}$  increase in nearly a power law manner with decreasing film thickness. These results clearly show that the decaying fields from the air and substrate surfaces constructively interfere with

one another thereby inducing full ordering in the P(S-b-d-MMA) at temperatures well above the bulk value of  $T_{\text{MST}}$ .

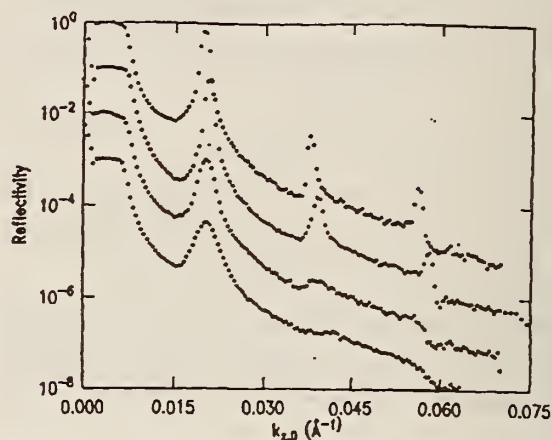


Figure 1. Neutron reflectivity as a function of the neutron momentum for a P(S-b-MMA) at different temperatures. Temperature increases as one proceeds from the uppermost to lowermost profile. The thickness of this specimen was 1.6  $\mu\text{m}$ .

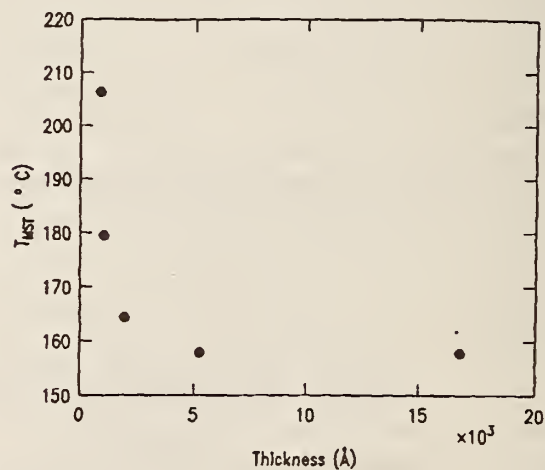


Figure 2. The variation in the temperature at which the copolymer films are fully ordered as a function of the film thickness.

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# NEUTRON REFLECTIVITY STUDIES ON COPOLYMER/HOMOPOLYMER MIXTURES

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S. K. Satija and C. F. Majkrzak

Thin films of symmetric diblock copolymers exhibit a near perfect orientation of the lamellar microdomains parallel to the surface [1,2,3]. This arises from the preferential interaction of the blocks with the substrate or air interfaces. The addition of small amounts of homopolymers, less than approximately 10 wt%, has been shown not to perturb the orientation of the lamellar microdomains [4]. Thus examining mixtures of a homopolymer labelled with deuterium with an unlabelled copolymer permits the investigation of the distribution of the homopolymers in the lamellar copolymer microdomains. In this work mixtures of perdeuterated polystyrene, d-PS, or perdeuterated polymethylmethacrylate, d-PMMA, of varying molecular weights with an unlabelled, symmetric diblock copolymer of PS and PMMA, denoted (PS-b-MMA), were investigated by neutron reflectivity. Specimens were prepared by spin coating the solution of the mixtures in toluene onto Si substrates. The films were annealed at 160 °C for at least 120 hr and quenched to room temperature.

Reflectivity measurements were performed on BT-7 at NIST up to value of the neutron momentum,  $k_{z,0}$ , of  $0.07 \text{ \AA}^{-1}$ . Figure 1 shows results for a mixture of P(S-b-MMA) with 10 wt% deuterated PMMA homopolymer ( $M_w \sim 5.7 \times 10^4$ ). The scattering length density profile shown in the inset was used to fit the measured reflectivity profile. Here it is clearly seen that the homopolymer segregates strongly to the center of PMMA microdomains. The system was modelled as alternating layers of PS and PMMA in which the PMMA layers contained some fraction of dPMMA homopolymer normally distributed within the domain.

The segregation of the PMMA homopolymer to the center of the domains indicates that the loss in entropy by confining the

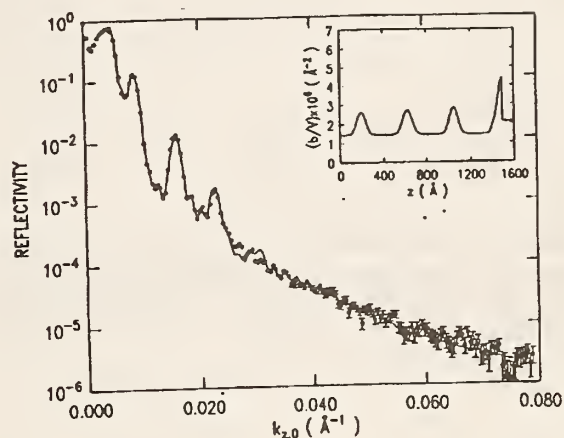
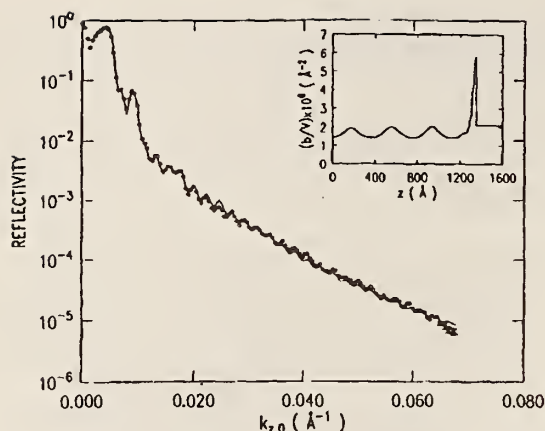


Figure 1 . Neutron reflectivity as a function of the neutron momentum for a mixture of 10 wt% d-PMMA ( $M_w = 5.7 \times 10^4$ ) with P(S-b-MMA) ( $M_w = 9.1 \times 10^4$ ). The solid line is the reflectivity profile calculated using the scattering length density profile shown in the inset.

homopolymer chains to the domain center is outweighed by that required to stretch the PMMA blocks to accommodate the homopolymer uniformly. In effect, the homopolymer chains are sandwiched between layers of the PMMA copolymer blocks. As molecular weight of the homopolymer decreases, the balance of the entropic effects allow better mixing within the domain. Figure 2 shows the reflectivity results for an analogous mixture in which the dPMMA molecular weight is reduced to  $1.2 \times 10^4$ . As is evident from the loss of strong Bragg reflections and the scattering length density profile inset, the low molecular weight homopolymer is better able to distribute within the domain, decreasing the contrast between the PS and PMMA layers. It is notable, however, that some segregation to the domain center is still apparent. It is also interesting to note that excess homopolymer appears to concentrate at the substrate surface in both systems.



**Figure 2.** Neutron reflectivity as a function of the neutron momentum for a mixture of 10wt% PMMA ( $M_w = 1.2 \times 10^4$ ) with P(S-b-MMA) ( $M_w = 9.1 \times 10^4$ ). The solid line is the reflectivity profile calculated using the scattering length density profile shown in the inset.

Experiments have also been done on systems with high molecular weight homopolymers ( $M_w \sim 5 \times 10^5$ ) added to the P(S-b-MMA). Interestingly, the analysis does not suggest a stronger confinement to the domain center in comparison with the  $5 \times 10^4$  mixtures of the same concentration. The results may indicate that the addition of high molecular weight homopolymer interferes with the copolymer ordering.

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## NEUTRON REFLECTIVITY STUDY OF A POLYMER-SOLID INTERFACE

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Polychlorotrifluoroethylene (PCTFE) is a semicrystalline polymer whose melting point is about 210 °C [1]. Because there are no hydrogen atoms in this polymer, its specific neutron scattering cross section is greater than that of a silicon crystal. Calculation indicates that a critical angle  $\Theta_c$ , for the polymer-Si interface is  $\sim 0.1^\circ$  using a 2.35 Å neutron wavelength. This particular polymer has very interesting properties and has been used as a model for studying amorphous to crystalline phase transition.

The experiments were performed at the BT-7 reflectometer at the NIST reactor. A graphite monochromator was used to select neutrons of a wavelength  $\lambda = 2.35$  Å with a width  $\Delta\lambda = 0.01$ . slit collimators reduced the incident beam divergence to  $0.016^\circ$ . The detector acceptance angle was set at  $0.975^\circ$ . single-crystal silicon wafers of 10 cm and 0.6 cm thickness were used as substrates. A

1.5 mm thick PCTFE film was placed in contact with each wafer. The wafer and polymer film were then sandwiched between two aluminum blocks containing heating elements. A vacuum of  $4 \times 10^{-6}$  torr was maintained throughout the experiments.

The raw data from a PCTFE-silicon interface at 240 °C is given in figure 1. The reflectivity of a free silicon surface (where the incident medium is air and not Si) is also presented in the same figure as a baseline. If the polymer density distribution at its interface with the silicon is uniform, the two reflectivity curves of figure 2 would coincide with each other since the critical angles for these two cases are nearly the same. The difference shown in figure 1 between the two reflectivity curves indicates that the density of polymer near the interface with the silicon is far from being uniform. This roughness could be attributed to some microvoids at the interface. Alternatively, it can be

considered likely that the polymer melt is in complete contact with the silicon substance so that the interface can be expected to be as flat as the silicon-air surface. The difference in reflectivity in this case might be attributed to a density fluctuation in the polymer melt near the interface. If one naively applies a Debye-Waller factor analysis of the diffuse scattering from a single rough interface [2,3] then the calculated magnitude of the roughness is about 60 Å RMS. The reflectivity measurement was also conducted at 255 °C which is 45 °C above the polymer melting point, and the result was identical to that at 240 °C suggesting no improvement in the interface uniformity by raising the temperature.

A series of measurements was carried out after cooling the sample to temperatures between 255 °C and 160 °C. At any temperature above 200 °C, no time dependence of the reflectivity was observed. In other words, by keeping the sample at any temperature between 255 °C and 200 °C, the polymer reached its equilibrium condition readily and the reflected beam intensity did not change with time. At 195 °C a long term drift of the intensity of the reflected beam in both the specular and the off-specular components was observed. At even lower temperatures, for example, 166 °C the reflectivity tended to stabilize within a few minutes. In figure 2 the reflectivity results of 236 °C, 202 °C and 166 °C were presented. The ordinate was shifted in order to highlight the difference among these three curves. These reflectivity results were reduced from the raw data by subtracting the off-specular component and then normalizing to the main beam intensities. Consequently, one can observe some interesting features in the reflectivity curves; more noticeable are (1) the shoulder at  $q = 0.02 \text{ Å}^{-1}$  in the melt (236 °C), (2) the sharpening of this shoulder at 202 °C, (3) the appearance of a maximum near  $q = 0.03 \text{ Å}^{-1}$ , (4) at 166 °C crystallization process is completed and all the features mentioned above disappeared.

A quantitative fit of the reflectivity results to a polymer segment density profile near the interface is in progress. The results demonstrate rather conclusively that the density of molten polymer near a solid surface is not uniform as in small molecule liquids. This nonuniformity

grows as the temperature passes the melting point then diminishes as the temperature is lowered further.

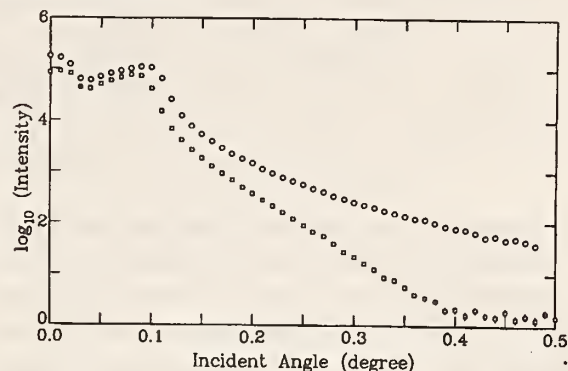


Figure 1. The raw neutron reflectivity results from the silicon-air interface (○) and the polymer-silicon interface (■).

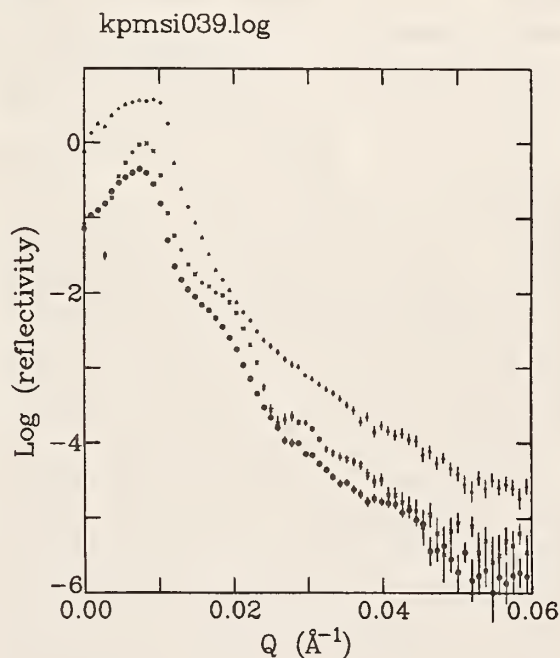


Figure 2. The corrected neutron reflectivity results from the polymer-silicon interface at three different temperatures, ● - 236 °C, x - 202 °C, ▲ - 166 °C.

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# SEGMENT DENSITY PROFILE OF GRAFTED POLYMER BRUSHES NEAR THE SOLID-SOLUTION INTERFACE

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Recently, considerable attention has been focused experimentally and theoretically [1-7] on understanding polymer brushes and their segment density profiles. Polymer brushes are polymer chains terminally attached onto a surface. When the surface coverage is high enough to allow overlap between chains, then the polymer chains are considerably stretched away from the surface. By using scaling and free-energy balance arguments, Alexander [7] was able to predict the equilibrium configuration of polymer brushes as a function of grafting density  $\sigma$  and chain length  $N$ . However, he assumed a uniform monomer density for the brush up to a distance  $h$ , the height of the brush. Later, Milner et al. [1] using self consistent field theory, obtained a density profile, for large  $N$  and in the highly stretched limit, which decays parabolically from the surface. Further numerical calculations by other groups [4,5] show that for small values of  $N$ , the parabolic profile is considerably rounded at the end near  $h = h_{max}$ .

The neutron reflectivity technique has been used with great success to study polymer formations at solution-air [11,12] solution-solid [13] and solid-solid [14] interfaces. Here we report on neutron reflectivity studies of end carboxylated polystyrene adsorbed on silicon surface in cyclohexane as a solvent. The carboxylated end is known to adhere well onto the silicon surface. Our results show the polymer segment density profile away from the silicon surface to be a parabolic density profile predicted for a grafted polymer brush by Milner et al. [1]. Two cases were studied: one with hydrogenated polystyrene (hps) and  $C_6D_{12}$  and the other with deuterated polystyrene (dps) with  $C_6H_{12}$ . The grafting density  $\sigma$  is such that the polymers were weakly in the brush regime. For a similar molecular weight of polymer the brush height for dPS- $C_6H_{12}$  is 50% higher than for hPS- $C_6D_{12}$ ,

which may be due to different  $\chi$  parameters for the two cases. For the longer brush, the segment density profile is a parabolic profile predicted for a grafted polymer brush. In the shorter brush, this parabolic profile is considerably rounded near the end. The experimentally measured and fitted reflectivity profiles are shown in figures 1 and 2.

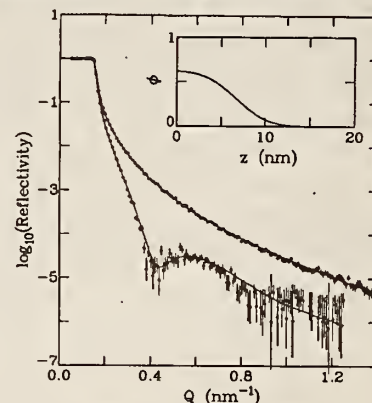


Figure 1. Open circles show reflectivity from pure  $C_6D_{12}$  near Si surface. Closed circles are the reflectivity from hps- $C_6D_{12}$  with the inset showing the fitted polymer segment density profile. The lines drawn are fits to the data as described in the text.

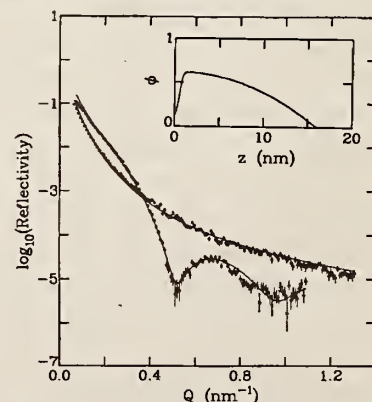


Figure 2. Open circles show reflectivity from pure  $C_6H_{12}$  near Si surface. Closed circles are the reflectivity from dps- $C_6H_{12}$  with the inset showing the fitted polymer segment density profile. The lines drawn are fits to the data as described in the text.

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## PHASE BEHAVIOR OF AQUEOUS POLY(VINYL-ALCOHOL) SOLUTION—A SMALL ANGLE NEUTRON SCATTERING STUDY

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The physical crosslinking of aqueous poly(vinyl alcohol) (PVA) solution in the presence of various anions such as borate, titanate, cupric and antimonate has been studied extensively [1]. In this work only the PVA-borate pair was included. The borate ion can attach itself to a PVA chain, and this process is called monocomplexation. Polyelectrolyte effects are expected from the monocomplexation. Through the formation of di-diols, the borate ion can also act as a reversible crosslink between two different chains or different parts of the same chain. The above process has been called di-complexation. In general, the monocomplexation gives rise to repulsive polymer-polymer interactions while the di-complexation induces attractive interactions. The concentrations of both the diol and the di-diol are determined by the chemical equilibrium of all the species involved. A self-consistent approach based on a Flory-type mean field theory has been developed by L. Leibler et al. [2] for determining these equilibrium constants.

The effective excluded volume interactions in the PVA-borate solution, as discussed in the foregoing paragraph, is made of three parts; the usual polymer-solvent interactions, the poly-

electrolyte interactions and the attractive interaction dues to di-complexation. Adding suitable amounts of borate salt at a given PVA concentration, one can increase the formation of didiol complexes leading to a clear-to-opaque transition. With further addition of the borate salt, the polyelectrolyte effect becomes dominant and this leads to a opaque-to- clear transition [3]. The purposes of this work are to determine (1) the effective excluded volume parameter, and (2) the corresponding changes in the radius of gyration across these transitions. Toward these goals, small angle neutron scattering (SANS) measurements were conducted in both the clear and the opaque regions. PVA solutions at two different polymer concentrations, one below  $C^*$  and one above  $C^*$ , were included.  $C^*$  denotes the polymer overlap concentration. For the samples with concen-trations above  $C^*$ , gelation set in before any of the clear-opaque-clear transitions. By comparing the results between samples at these two concentrations, one can determine the effect of gelation on the changes of both the effective excluded volume parameter and the radius of gyration across these transitions. Deuterated and protonated PVA with a degree of polymerization (DP) of 1100

were used. The overlap concentration,  $C^*$ , was determined to be about 1.5% wt. based on viscosity measurements. The value of  $C^*$  showed a modest decrease with increasing boric acid concentration. Two polymer concentrations used in this work were 1.25% wt. and 2.0% wt. and the NaOH content was held at 0.167 M for all the specimens.

The SANS measurements were conducted at the NIST reactor with the wavelength set at 9 Å.

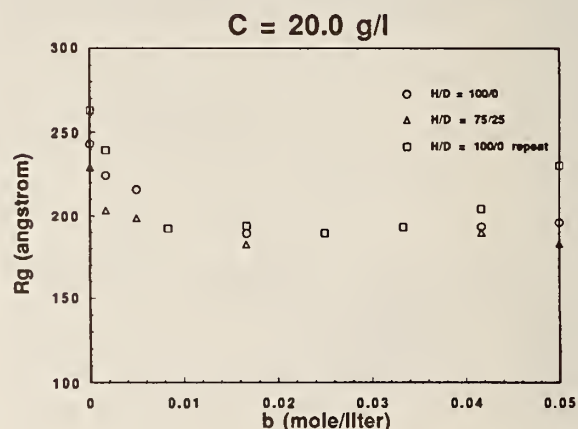
The values of  $\chi$  obtained from SANS are listed in table 1; for both polymer concentrations the value of  $\chi$  reached a maximum at an intermediate concentration of boric acid. Concurrently, the samples turned opaque. For all the clear solutions and gels, the value of  $\chi$  was always below 0.5, whereas for the opaque samples the corresponding value was greater than 0.5.

The change in radius of gyration of the 20 g/l samples are given in figure 1. The results clearly show that the chains collapse somewhat in the opaque region which exists between  $[b]$  of 0.01 M to 0.04 M. It is noteworthy that the polymer concentration is above  $C^*$  and the clear-opaque-clear transition occurs in a gel state. The present results demonstrate that gelation, at least physical gelation, does not inhibit the collapse of individual chains. The results from 12.5 g/l sample is identical to figure 1; the collapse of chains coincides with the clear-opaque-clear transition.

In summary, the SANS result demonstrated that the complex polymer-solvent interactions which exist in borate-PVA solution can be adequately lumped into a single parameter. In addition, the constraint of gelation did not inhibit individual chains from an expansion-collapse-expansion transition as the solution underwent a clear-opaque-clear transition.

**Table 1.** The effective polymer-solvent interaction parameter from SANS data. c - clear, o - opaque, s - solution, G - gel

		POLYMER CONCENTRATION	
		0.01245	.020
	0.	0.461 (CS)	0.440 (CG)
	.00167	0.466 (CS)	0.444 (CG)
	.0050	0.480 (CS)	0.456 (CG)
	.00833	0.534 (OS)	
Boric Acid (M)	.0167	0.530 (OS)	0.521 (OG)
	.0333	0.468 (CS)	
	.0417	0.442 (CS)	0.456 (CG)
	.05	0.440 (CS)	0.452 (CG)



**Figure 1.** The change in the radius of gyration of PVA chains as they underwent a clear- opaque-clear transition within a gel state. The transition points are at 0.01 M and 0.04 M of boric acid. Results from three sets of data were presented in this figure.

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## DIFFUSE SCATTERING IN ICOSAHERAL PHASE ALLOYS

J. L. Robertson

Diffuse scattering is observed beneath the groups of strong peaks in the powder diffraction patterns of all the rapidly quenched icosahedral phase alloys studies thus far, including those thought to be free of phason strain (e.g., i-AlLiCu and i-AlRuCu). In the case of i-AlMnSi such diffuse intensity is found at  $Q^* \approx 2.8 \text{ \AA}^{-1}$ ,  $3.5 \text{ \AA}^{-1}$ ,  $5.0 \text{ \AA}^{-1}$ , and  $5.8 \text{ \AA}^{-1}$  (fig. 1e) which seems to resemble closely the main features of the amorphous diffraction pattern [1,2]. The results of recent work centered on modeling the structure of i-AlMnSi by a pseudo-random packing of icosahedrally symmetric atomic clusters [3,4] show that these features are reproduced in the calculated powder diffraction pattern without including either the "glue" atoms (atoms that fill the space between the clusters) or any substitutional disorder within the atomic clusters. Here the diffuse intensity is clearly visible in the total intensity calculated from the model (fig. 1d) although it does not seem to be in the undecorated  $S(Q)$  (fig. 2).

At least for i-AlMnSi, this must result from weak peaks with large  $Q^\perp$  that are part of the background in the undecorated  $S(Q)$  [5] but are heavily weighted in the Al-Al partial intensity (fig. 1b). This has been confirmed by a calculation of the structure factor for a single MacKay icosahedron (fig. 3) in which strong broad peaks appear in the Al-Al partial intensity at  $Q^* \approx 3.0 \text{ \AA}^{-1}$  and  $5.0 \text{ \AA}^{-1}$  which are not in the Mn-Mn and Mn-Al partials. At these  $Q$  positions, however, the strong Al-Al contributions appear in symmetry directions where the "Bragg" peaks due to the model "lattice" are weak (i.e., large  $Q^\perp$ ). Figure 4 shows that the Al-Al structure factor for a single cluster peaks in the threefold symmetry direction (at  $Q^* = 2.85 \text{ \AA}^{-1}$ ) while the strong quasicrystal peaks at this value of  $Q$  are in the twofold and fivefold symmetry directions; thus the weaker (and therefore broader) peaks in the threefold directions are more heavily weighted and appear as "diffuse" scattering in the measured powder patterns.

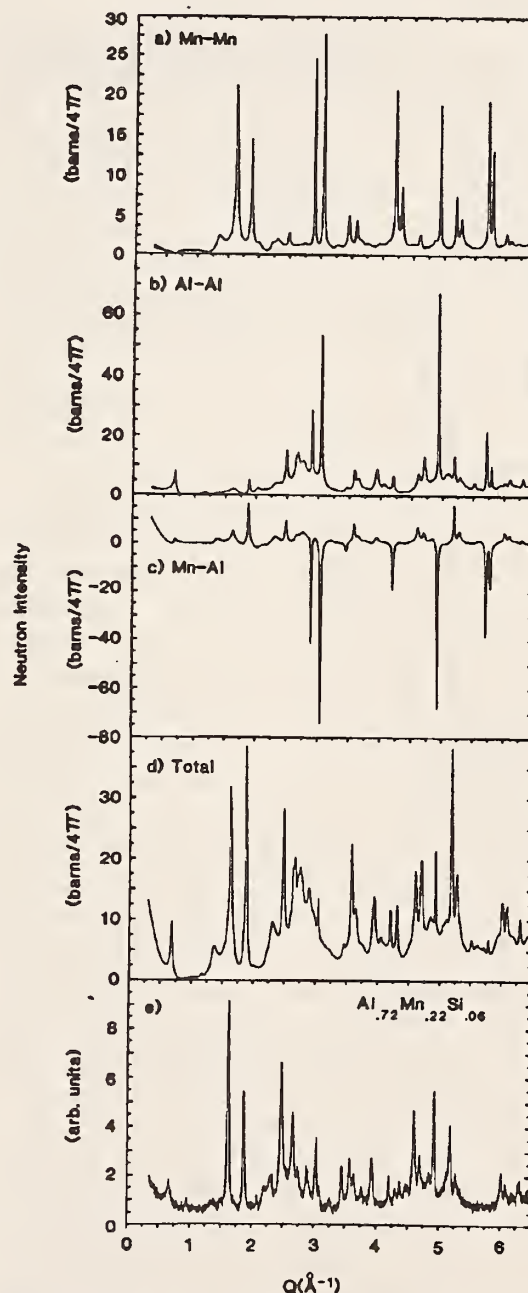


Figure 1. Partial neutron scattering intensity calculated for (a) Mn-Mn, (b) Al-Al, and (c) Mn-Al correlations; total neutron intensity (d) and experimental neutron intensity data (e) on i-AlMnSi [6].

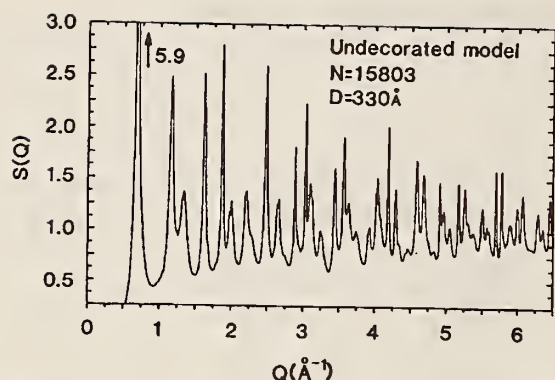


Figure 2. The calculated  $S(Q)$  for the undecorated model.

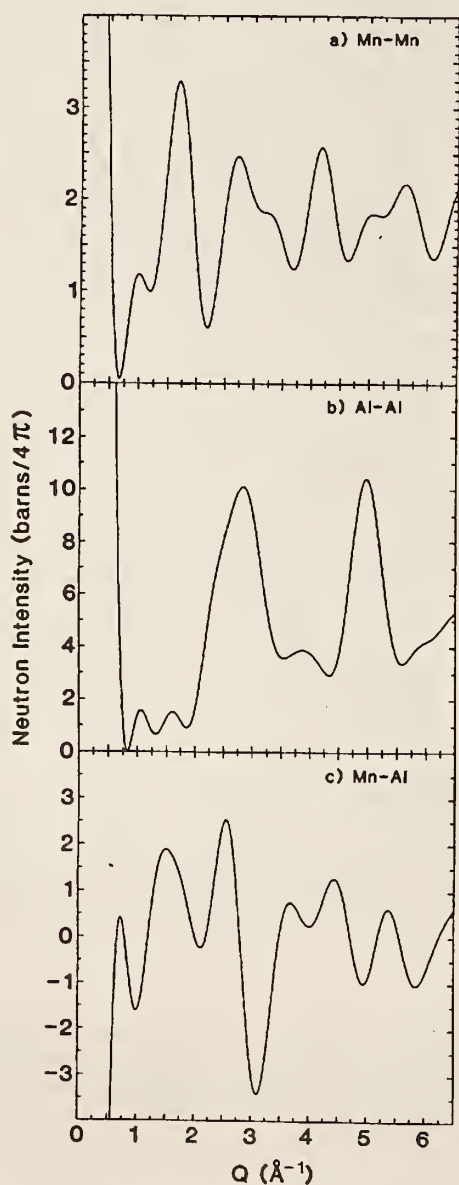


Figure 3. Partial neutron intensities for a single AlMnSi atomic cluster. (a) Mn-Mn, (b) Al-Al and (c) Mn-Al.

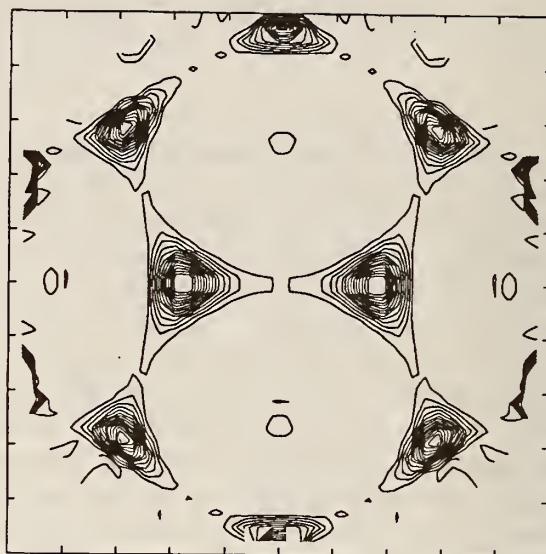


Figure 4. Al-Al partial intensity distribution for a single cluster at  $Q = 2.85 \text{ \AA}^{-1}$ ; half of reciprocal space is projected onto the plane along a twofold symmetry axis.

Current efforts are directed towards calculating the "single crystal" diffraction patterns from the (atomic) decorated model to determine the distribution of the "diffuse" intensity in reciprocal space.

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## TEXTURES OF TANTALUM METAL SHEETS BY NEUTRON DIFFRACTION

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and

H. J. Prask

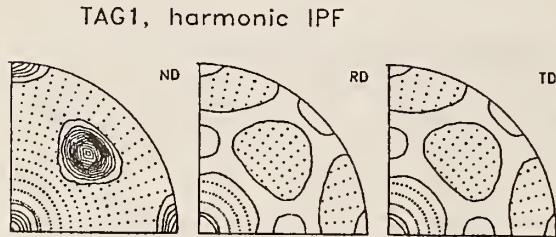
The orientation distributions of five different samples, TaPA, TaG1, TaG2, TaQ2-S1 and TaQ2-S4, were studied by neutron diffraction. The TaPA specimen is a commercial Ta sheet with an unknown fabrication history. The TaG1 and TaG2 specimens were fabricated by uniaxial compression along the cylinder axis direction, with 90% reduction in two steps at room temperature. The TaQ2 specimens were made by the same forging process except the 90% reduction was achieved in three steps. TaQ2-S1 is the section closer to the center of the forged disk and S4 is the adjacent section at the periphery side. The pole figure data of 200, 211, 220, 310 and 222 were collected at the BT-6 neutron diffractometer. The ODF (Orientation Distribution Function) analyses were performed using the WIMV and harmonic methods of the program POPLA [1] for the TaPA and the TaG type samples, and using WIMV for the TaQ2 samples.

The texture of TaPA consisted of three components: dominant  $\{100\}\langle 010 \rangle$  cube texture and weaker  $\{111\}\langle 112 \rangle$  and  $\{111\}\langle 110 \rangle$  texture. Since  $[112]$  is the TD (Transverse Direction) component of  $(111)[1\bar{1}0]$  and  $[1\bar{1}0]$  is the TD component of  $(111)[11\bar{2}]$ , it is conceivable that the TaPA sample was fabricated by cross rolling. The cube texture found in the sample is considered to be a serious disadvantage for the deep-drawing application, because it produces extremely anisotropic physical properties. The cube texture has been observed in many FCC metals and alloys after primary recrystallization annealing in certain temperature ranges. Recently, cube texture has been found also in BCC metals [2,3,4].

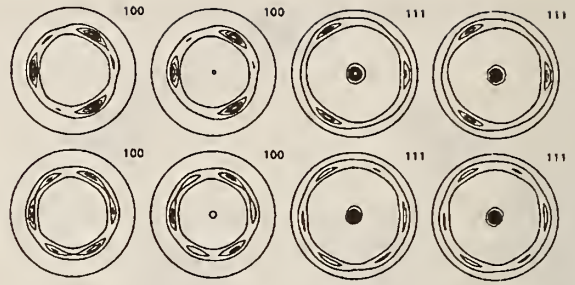
The TaG type specimen textures were dominated by  $[111]$  and  $[100]$  fiber axes. The ODF analyses, using the two different methods, yielded essentially identical results. The inverse pole figures of the ND (Normal Direction), RD (Radial Direction), and TD (Transverse Direction) of TaG1 sample obtained by the

harmonic method are presented in figure 1. The pole figures of the two TaQ2 samples showed a pseudo threefold rotation symmetry about the ND and a pseudo twofold symmetry about the RD, as shown in figure 2. The ODFs were analyzed with a triclinic sample symmetry. The ND inverse pole figures of the two TaQ2 sections were totally dominated by 111 poles. The crystallite orientation distributions of the TaQ2 were a mixture of fiber texture and sheet texture types, with different components of sheet texture depending on the radial distances. The S1 texture consisted of two components,  $\langle 111 \rangle$  fiber and  $\{111\}\langle 11\bar{2} \rangle$  sheet type. S4 contained an additional texture  $\{111\}\langle \bar{1}\bar{1}2 \rangle$ , and had a higher degree of fiber texture than the S1 sample. Texture development by uniaxial compressions was found to be quite sensitive to the number of strikes in the forging process. The sample with two strikes (i.e., TaQ2-S1) produced an ideal  $\langle 111 \rangle / \langle 100 \rangle$  double fiber texture, with the fiber axes parallel to the compression direction. On the other hand, the sample with three strikes (i.e., TaQ2-S4) produced a hybrid texture consisting of  $\langle 111 \rangle$  fiber type and  $\{111\}\langle 11\bar{2} \rangle$  sheet type texture (with additional  $\{111\}\langle \bar{1}\bar{1}2 \rangle$  near periphery of the compressed disk). The degree of texture was much larger in the three-strike sample, with the texture index of 4.6 for section-1 and 5.7 for section-4 versus 2.5. Such definitive difference in the texture formations suggests an entirely different plastic flow in the two forging processes. The 90% reduction by the two strike forging delivers a much larger impact pressure than the three strike forging. The friction between the tool and the sample surface becomes larger with increasing compression, particularly around the periphery of the sample because of lubricant break down, which could affect the strain distribution in the sample. The textures of the TaQ2 sample have a text-book case radial symmetry which is consistent with the plastic flow in the plane-strain compression. The amount of the radial strain, in the friction-free

plane-strain compression, increases linearly with the radial distances, and is believed to be the main cause of the different texture formation in sections #1 and #4 of TaQ2.



**Figure 1.** The inverse pole figures of TaG1. The contour levels are given in 1 mrd (Multiples of the Random Distribution) intervals. The regions lower than 1 mrd are marked with dots.



**Figure 2.** Observed and calculated (100) and (111) pole figures of TaQ2-S1 (top row) and TaQ2-S4 (bottom row). The contour levels are given in 4 mrd steps starting from 1 mrd up to 49 mrd.

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## RESIDUAL STRESS DETERMINATION IN A STEEL FATIGUE-TEST SPECIMEN

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and

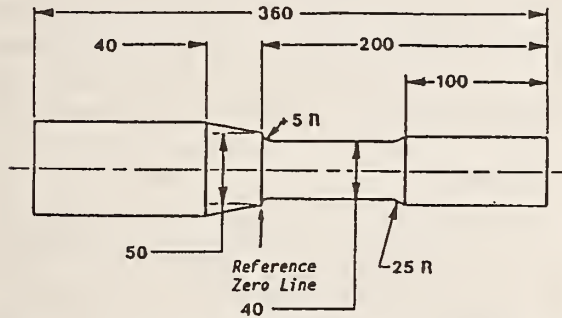
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The Society of Automotive Engineers Fatigue Design and Evaluation Committee has been conducting a long-term program aimed at the development of a predictive capability for fatigue life in which the multiaxial fatigue behavior of induction-hardened and tempered SAE 1045 notched shafts is being examined. A comprehensive, integrated engineering approach is being applied to the problem: it includes materials properties characterization, finite element analysis prediction of stress/strain, residual stress characterization, fatigue-life measurement, and fatigue lifetime prediction. Some depth-profiling of residual stresses has been done by x-ray diffraction with layer removal [1]; however, the nondestructive character of neutron diffraction offers a unique

means for both characterizing the residual stress distributions and in testing the x-ray layer-removal approach.

The geometry of the component-like test "axle" is shown in figure 1. An unfatigued and a fatigued (to ~ half of fatigue life) axle were studied. Because of induction hardening of the surface region in these samples, the near-surface region (0 - 3 mm depth) is predominantly tempered martensite, changing to a mixture of pearlite/ferrite at ~ 10 mm depth. To determine the reference  $d_0$ 's for these regions, a third axle was cut by EDM into a 3 mm thick "martensite" ring which included the surface, and a shaft-centered 20 mm diam pearlite/ferrite plug, each 1 cm wide.

For all of the measurements the (110) reflection of steel was employed at a scattering angle of  $80^\circ$  from the sample. The  $d_0$ 's for the martensite and pearlite/ferrite structures were obtained from the ring and plug pieces, respectively, with  $2 \times 2 \text{ mm}^2$  apertures and the macroscopic equilibrium conditions for axial stresses. Diffraction elastic constants ("XEC") determined by Prevey [2] for SAE 1050 steel were used.



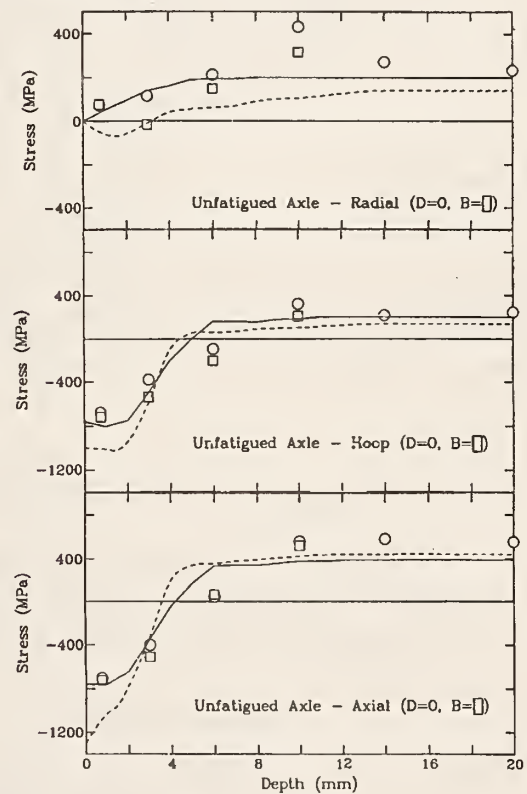
**Figure 1.** SAE biaxial fatigue test "axle". The 120 mm length on the left is the "grip" in fatigue test cycling. The diameters at the left and right ends of the axle are 63.5 and 43 mm, respectively.

Apertures ranging from  $1 \times 5 \text{ mm}^2$  to  $6 \times 6 \text{ mm}^2$ , as detailed in reference 3, were used. Data were obtained along single radii at positions "B" (= 10 mm from the reference zero line (fig. 1)) and "D" (50 mm away) in the unfatigued shaft; at "B" and "D" on the radii parallel to the bending direction, and at the "B" position at  $90^\circ$  from the bending direction in the fatigued axle. All d-spacing data were normalized to  $d(110)$  of an iron powder which was scanned for each change of apertures.

A test of the ring-plug  $d_0$ 's was made using the unfatigued axle data at the "D" position. Using the hardness vs. depth results of Langner [4] as a measure of the percent martensite,  $d_0$ 's for each depth examined by neutrons can be inferred, with the ring-plug  $d_0$ 's at the extremes. The axial stresses at the D position in the intact unfatigued axle as determined from neutron diffraction balance to 10 MPa. This means that perfect balance would be achieved if the axial stress determined at each of the six measurement points was shifted by 10 MPa. Since the standard deviation on each measured axial stress value is typically  $\sim 20 \text{ MPa}$ , this balance-of-

stresses represents an excellent confirmation of the approach.

Ochsner [5] has made a finite element analysis (FEA) of an induction hardened steel shaft to obtain the residual stress distribution. The results are shown in figure 2 along with the neutron-diffraction-determined stresses at positions "B" and "D" in the unfatigued shaft. The effect of fatigue on the residual stress distributions is illustrated in figure 3 where results for the two shafts are shown at corresponding positions.



**Figure 2.** Neutron diffraction determined residual stresses for the unfatigued axle compared to the finite element analysis [5]. The dashed line is the FEA result at 5 mm from the reference zero line; the neutron "B" values are at 10 mm.

In summary, the FEA results are in reasonably good agreement with the stress measurements for the unfatigued axle. However, much less "B"- vs. "D"-position difference than the FEA predicts is observed. No FEA results are yet available for the fatigued-axle case. Experimentally, the measurements at the "D" position show very little stress relaxation with fatigue except at 10

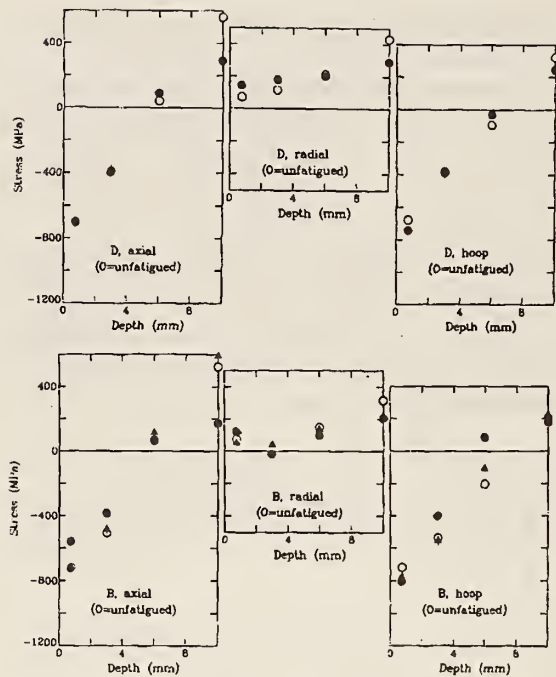


Figure 3. Neutron diffraction determined residual stresses at the 10 mm ("B") and 50 mm ("D") positions for the fatigued (●) and unfatigued (○) samples. The triangles correspond to stresses at a radius 90° to the bending axis.

mm depth for  $\sigma_{zz}$ . Except at this depth, there seems to be a tendency for the axial and hoop stresses to become more tensile with fatigue at the "B" position. At the "B" position, the stresses measured with neutrons at 90° to the bending direction are very close in magnitude to the unfatigued stresses, as expected.

An additional, important result of this study is a confirmation of the validity of x-ray diffraction with layer removal as a means of residual stress vs. depth determination for a cylindrically-symmetric specimen [1]. A detailed comparison shows very good agreement for the two techniques for all residual stress components [3].

#### References

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## NEUTRON ACTIVATION AUTORADIOGRAPHY OF PAINTINGS

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and  
W. Leuther and C. O. Fischer (Hahn-Meitner Institute)

Neutron activation autoradiography applies neutron activation analysis and film autoradiography to the study of oil paintings. The results are based on the pigment selection and painting techniques utilized by the artist to manifest a unique style. The method helps to gain an insight into the artist's creative process through the revelation of characteristic brushstrokes, underdrawings and alterations. Sensitive x-ray films are used to record the images processed by the decay of radioactive components in the painting following activation. The darkening of the film is mainly the result of beta-particle emission. Gamma ray spectroscopy helps in the interpretation of the autoradiographs by providing elemental analysis.

Multiple autoradiographic exposures are generated for each painting to isolate the images created by groups of isotopes with different half-lives. Films serve as convenient, high resolution area detectors for the registration of the painting's radioactivity. However, only twelve timed exposures can be made in a typical painting study due to the low efficiency of the film system. Ten of the exposures are created during the first two weeks of film exposure with the period of exposure being about equal to the time after activation of the painting.

Research was conducted to improve the radioactivity detection of the autoradiography process. A more efficient system could provide better quality autoradiographs and thereby

enhance the opportunity for interpretation. Also, a more efficient system could reduce the radiation exposure needed for the activation of the painting. We are presently activating the painting for 20 to 30 min at  $3 \times 10^2$  neutrons/cm<sup>2</sup>/sec. This exposes the painting to between 300 and 500 rads of gamma radiation as determined by measurements made using TLD detectors at the thermal column where the paintings are activated.

An experiment was carried out to test the usage of light scintillation screens for film speed enhancement. Kodak XAR Films, recommended by the manufacturer for autoradiography use, were used throughout the experiment. The film-screen combination is commonly used in medical x-ray applications. However, the effect on beta-particle detection is not well known. For the experiment ten different scintillation screens were used. The screens were selected for their light emission spectrum, resolution and physical properties (thickness, light transparency). Gold foils were activated to simulate a pigment in a painting. Column A in table 1 shows the film density readings for various film screen combinations.

**Table 1.** Film density readings showing effect on speed enhancement and light output of various scintillation screens.

Scintillation Screen Type	Film Density in D <sup>+</sup>	
	A	B
Rego Detail	1.27	0.26
Rego Universal	2.35	0.27
Rego Special	2.62	0.25
Rego NPU	2.74	0.42
Rego NPR	2.82	1.00
Rego GR2	2.28	0.23
Rego GR4	2.52	0.33
Rego GR6	2.51	0.25
Kodak Lanex Fast Thin	2.56	0.21
Kodak Lanex Fast Thick	2.70	0.12
No Screen	1.28	

<sup>+</sup>D = log  $\tau$ , where  $\tau$  is film transparency.

The results show the efficiency of the current no-screen film system can be improved by selecting a proper film screen combination. It is characteristic that within the normal useful range of x-ray film the density reading is linearly

proportional to the logarithm of exposure time. Based on the data presented and extrapolating from typical plots for Kodak film of density versus log of exposure time, the use of Rego NPR screen with film can be seen to reduce the necessary exposure time ten fold or more over the current no-screen film practice. A more precise speed enhancement factor will be determined by generating the specific film response characteristics with respect to beta particle exposures. It will also be important to investigate the effect of different beta particle energies on the speed enhancement factor. Efforts are now being made to obtain a large size screen on flexible backing fabricated for autoradiography use.

Another objective of the experiment was to study the feasibility of converting radioactivity into visible light through scintillation screens in order to capture the light output by electronic video means. This was to prepare for the eventual change to a film-less autoradiography system.

Typically, a gold beta particle fluence of  $1 \times 10^6$  /cm<sup>2</sup> is required to darken film to a 1D reading. A density of 1D allows detection of differences of 3%. To allow equivalent differences to be distinguished in a filmless system requires  $1 \times 10^3$  photons/cm<sup>2</sup> (3% counting statistics). Therefore an electronic light photon detection system can in principle improve the present efficiency by as much as three orders of magnitude and at the same time usher the autoradiography technique into a new age by incorporating computer image processing advancement.

For the experiment the light output from each scintillator was recorded by placing a film on the back side of the scintillation screen to simulate detection through the screen to an electronic detector. The density readings from the various screens are listed in column B of table 1. Column B in table 1 indicates the same rego NPR screen also generates the most light. Future tests regarding photon detection will use NPR screens of various thicknesses with more transparent backing.

## D. NUCLEAR ANALYTICAL CHEMISTRY

### NUCLEAR METHODS GROUP: OVERVIEW

R. R. Greenberg (Inorganic Analytical Research Division)

The development and application of nuclear analytical techniques for elemental compositional analysis of greater accuracy, higher sensitivity and better selectivity are the goals of the Nuclear Methods Group. A high level of competence has been developed in both instrumental and radiochemical neutron activation analysis (INAA and RNAA). In addition, the group has the capability of using neutron beams as analytical probes with both prompt gamma activation analysis (PGAA) and neutron depth profiling (NDP). NDP determines concentrations of several important elements (isotopes) vs. depth profiles within the first few micrometers of a surface by energy analysis of the prompt charged-particles emitted during neutron bombardment. PGAA, on the other hand, measures the total amount of an analyte present throughout a sample by the analysis of the prompt gamma-rays emitted during neutron capture. These techniques (INAA, RNAA, PGAA, and NDP) provide a powerful combination of complementary tools to address a wide variety of analytical problems of great importance in science and technology.

The use of a variety of nuclear methods has continued to contribute to the Standard Reference Material (SRM) certification effort; this year's efforts include measurements performed on a number of SRMs including: Fly Ash, Coke, Sewage Sludge, two (used) Automobile Catalysts, Apple Leaves, Peach Leaves, Tomato Leaves, Bone Ash, Bone Meal, Water, Grass, Boron in Silicon, two Wear Metals in Oils, and three Soils. Group members are serving as Technical Champions for several of these new SRMs, and as such are responsible for scientific decisions made throughout the production and certification processes of these materials. Members of the Nuclear Methods Group have also collaborated with researchers from the Microanalysis Group (837) in developing a boron depth-profiling SRM.

Optimizing the counting conditions in the various forms of NAA can generally improve

precision and/or increase sample throughput. This is especially important when counting low-activity materials. Much can be gained in sensitivity by using high-efficiency detectors. With care in selection of shielding material and detector, the only important source of gamma-ray background, other than the sample and the materials from which the detector shield is constructed, is the interactions of cosmic ray particles with the shield and the detector itself. As part of our continuing efforts to improve the NAA method we have performed experiments to apply Cooper's figure of merit for detector performance to two excellent modern detectors. The results obtained shows that for the ultimate sensitivity in quantitating a simple spectrum, high efficiency overwhelms good resolution, low background, or any other criterion of detector quality for a given measurement. In practice, however, the choice is not so simple, i.e., when summing corrections are large, when unresolved multiplets are present, when the total count rate is high, when background lines (not continuum) are important, when sample-detectors positioning uncertainty limits the accuracy, or when requirements of sample shape dictate the counting configuration. Long-term studies of such problems are under way.

The Biomonitoring Specimen Bank Research Project continued to support other agencies' monitoring programs. These programs include the EPA Human Liver Project, the NOAA National Status and Trends (NS&T) program, the NCI Micronutrient program, the IAEA/NIST/FDA/USDA Total Diet Study, the NOAA Alaska Marine Mammal Project, and the National Marine Mammal Tissue Bank. Research has centered on specimen banking protocols and improved analytical methodology. The group's participation in intercalibration exercises with the project participants and the development of QA materials for various marine analyses has helped to enhance the quality of the analytical results used in the assessment of the environmental health of the nation. This year,

## NUCLEAR ANALYTICAL CHEMISTRY

the group has provided trace element measurements (for information values) in SRM 1974 (Organics in Mussel Tissue). This material is the first NIST frozen tissue homogenate available with concentrations given for both trace elements and trace organics. In addition, as part of the marine mammal projects, we have prepared a whale liver quality control material for use by other laboratories involved in marine mammal tissue measurements. The analytical experience gained from these measurements will be used to develop new SRMs for marine mammal tissues in the future.

The joint NIST/FDA/USDA study of trace elements in human diet, sponsored by the International Atomic Energy Agency, has completed its sixth year. A total of 275 diets from different countries have been analyzed to date for minor and trace elements. Preliminary data evaluation shows some interesting differences, among the countries studied, in the daily dietary intakes for several elements such as As, Hg and Se. Ten diets from different regions of the United States have also been collected, and thus far, seven have been analyzed. The data obtained from the U. S. diet composites have confirmed daily intake results for some of the elements investigated by the FDA (based on individual food analysis), as well as established reliable daily dietary intakes for additional elements including B, Cr, Cs, Li and Sn. In the case of Li, the observed intake values are considerably lower than earlier published results. In addition, multiple diets from Spain, Italy and Turkey have been analyzed for B and Li. The results show considerable variation in the daily dietary intakes among the three countries.

The collaboration with Brian Clarke of McMaster University on neutron activation-mass spectrometry has continued to provide valuable information on ultratrace levels of boron and lithium. A wide variety of materials was investigated this past year, and results were obtained for boron and lithium concentrations in several different protein components in blood, various individual foods, and a number of geological reference materials. These analyses have resulted in numerous publications as well as a certified value for Boron in the Total Diet SRM.

The group has taken an active role in the NIST program on high-temperature superconductivity research, both in the measurement of impurities in starting materials and final products, and in determination of the stoichiometry of metallic constituents. The effort this year has centered on the development of accurate, rapid measurements of these materials by both NAA and PGAA. An effort to establish an accurate, monitor activation analysis technique for further study of high temperature superconductors at NIST is under way.

Nearly a decade ago a systematic error for PGAA was observed in which element sensitivities (cps/mg) increased with increasing H concentration. The process responsible for the observed enhancements is neutron scattering by hydrogen within the sample. Experimental studies have shown that PGAA element sensitivities are dependent upon the scattering density (or hydrogen concentration), as well as the sample shape. Consistent with these results, Monte Carlo calculations have demonstrated that, depending on the absorption and scattering power of the sample, and on the sample size, shape and orientation with respect to the neutron beam, scattering within the sample may either increase or decrease the neutron path length in the material and thus may change the probability of neutron absorption. Therefore, an analytical signal, which follows an absorption reaction, is also a function of these variables. Theoretical work and Monte Carlo calculation experiments have demonstrated that for spherical samples, neutron scattering serves to mitigate the effects of neutron self-shielding, and produces no additional enhancement. PGAA measurements on spheres have confirmed this theory and have comprised the majority of the measurements performed in the past year. For most materials (e.g., paraffin, urea, SRM 1632a, SRM 1577) results show that element sensitivities for disk-shaped samples (of constant H concentration and diameter [12.7 mm]) vary with thickness over the range of 2 - 12 mm, but that sensitivities remain constant for spheres of the same materials (diameters 2-12 mm). The sensitivity values for the spheres compare well with those obtained from measurements on nonhydrogenous standards, indicating that sensitivity enhancements are eliminated by using spheres.

However, for some materials (aqueous solutions of Gd and Sm), sensitivities were not constant over the same range of sphere diameters. To insure accurate data interpretation for such samples that both strongly absorb and strongly scatter neutrons, standards should be matched as closely as possible to the samples with respect to both the amount of scatterer and the amount of absorber.

During the past year, a large part of the group's efforts has been directed at the exploitation of the analytical applications of cold neutrons. These efforts are needed to take full advantage of the guided cold-neutron beams now available at the new Cold Neutron Research Facility (CNRF). The group's involvement has been to design and construct state-of-the-art instruments for both PGAA and NDP using cold neutrons. The group's efforts have been aided substantially by the ability to use an existing cold neutron beam at the KFA Jülich facility. A new chamber for the cold neutron depth profiling (CNDP) instrument has been installed at the NIST Cold Tube West (CTW) location in the confinement building. The 60-cm diam chamber has ultra-high vacuum capability, and has been designed to be adaptable to many different types of experiments. The final configuration allows remote scanning of 15 x 15 cm samples and rotation of both sample and detector angles relative to the beam. Sample movements are controlled by a desk top computer. Using the new instrument, the first  $^{17}\text{O}$  depth profiles have been made in collaboration with the Eastman Kodak Company. These measurements were made on a cobalt nickel oxide produced using enriched  $^{17}\text{O}_2$  gas.

A permanent, full-time instrument for prompt-gamma activation analysis (PGAA) has been constructed as part of the Cold Neutron Research Facility. This new facility will allow accurate measurements of low levels of many elements including hydrogen. Hydrogen backgrounds of a few tens of micrograms have already been achieved. This promises to be of value in numerous applications where quantitative, nondestructive analysis of small quantities of hydrogen in materials is necessary. Further background reduction by one to two orders of magnitude is probable in the near future. Sensitivities (counting rate per gram of

analyte) of a number of elements have been compared using the new cold-neutron instrument to those obtained with the thermal Maryland-NIST PGAA instrument. At the same reactor power, sensitivities for most elements are a factor of four to six better with the cold-neutron apparatus as a result of a compact sample-detector geometry. The first quantitative measurement with cold neutron PGAA in the CNRF was the determination of hydrogen in a sample of  $\text{C}_{60}$  fullerene "buckyballs" intended for neutron scattering studies. The sample was found to contain  $0.077 \pm 0.014$  wt % H, which was adequately low for the neutron scattering measurements. In addition, hydrogen was sought in a 50-nm borophosphosilicate glass film on one fourth of a 10-cm silicon wafer; an upper limit of  $2 \mu\text{g}/\text{cm}^2$  was found.

A long-range program to explore and develop the analytical applications of focused beams of cold neutrons has been initiated within the group. The ultimate goal of this research is to produce beams of neutrons which have intensities several orders of magnitude greater than previously available. Such beams will greatly enhance the capabilities of both PGAA and NDP, and may ultimately lead to a neutron probe for microanalysis. The neutron micro-guide appears to be one promising approach to achieve analytically useful focused neutrons. As a first approach, a device will be developed and tested using a stack of ultrathin, nickel-coated single-crystal silicon wafers as focusing elements. The silicon wafers act as the transmission medium for the neutrons, which reflect from the 1000 Å nickel surface coatings. The superposition of the individual outputs becomes the focal point. One hundred of these wafers have been obtained for tests of this first focusing element.

The wafers have been characterized with X-ray reflectivity measurements at a synchrotron source. Cold-neutron measurements using a polychromatic beam at CTW have shown that these wafers can deflect the neutron trajectories successfully. More precise measurements have been performed using monochromatic neutron beams at BT-7 (NIST) and at ILL, Grenoble. These measurements, some of which include up to eleven reflections, have shown a high degree of reflectivity for the silicon-nickel interface.

Another focusing concept involves the use of capillary optics, a concept which has proven successful with X-rays, and which allows for the possibility of two dimensional focusing. In collaboration with scientists from the USSR and SUNY-Albany, we have begun testing this concept with cold neutrons. We have obtained a number of capillary fibers, each containing over a thousand individual channels within a glass diameter of less than one millimeter, and have observed the transmission (and deflection) of cold neutrons through an array of such capillaries bent to radii of curvature as small as 0.4 meters.

The strong interaction with industrial scientists using NDP, PGAA, and NAA has continued during the year with a growing number of guest workers, research associates, and joint publications. For example, working this year with researchers from Texas Instruments, we have used NDP to study various aspects of quality control using CVD (chemical vapor deposition) reactors. These measurements will be useful in optimizing process yield and reliability.

The Nuclear Methods Group is also collaborating with scientists from the NIST Physics Laboratory in a new measurement of the neutron lifetime. The technique used involves detecting the protons which decay in a neutron beam passing through a superconducting-magnet proton trap. Current efforts are concentrating on lowering the uncertainties due to neutron fluence rate measurements, one of the largest components of the uncertainty in the measurements we reported last year. A gamma-alpha coincidence

technique is being used to eliminate the dependence on detector efficiency. A counting system with two germanium detectors and one alpha detector has been installed at neutron guide NG-6. Preliminary measurements are currently in progress.

During the coming year the group will continue to improve the accuracy, sensitivity and productivity of nuclear methods as applied to elemental composition measurements. Problems to be addressed include those inherent in sample preparation, irradiation, radiochemical separation, counting and data reduction, with the goal of minimizing and quantifying various sources of random and systematic errors in analysis by nuclear methods. Maintaining full accuracy at high count rates using current generation data acquisition electronics is the goal of our count rate dependent studies. Accurate quantification of gamma-ray self-absorption and measurement of the shape of the efficiency curve are required for accuracy in monitor activation analysis (since matching of sample with primary standards is not required). In addition to allowing rapid sample turnaround with minimum sacrifice of accuracy, monitor activation analysis also provides good quality control when used in parallel with traditional primary standard NAA.

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## DETERMINATION OF TRACE ELEMENT IMPURITIES IN HIGH TEMPERATURE SUPERCONDUCTOR STARTING MATERIALS

D. A. Becker (Nuclear Methods Group)

In recent years the entire field of superconductivity has been revolutionized by the discovery of Bednorz and Muller of IBM that certain types of metallic oxides become superconductive at about 35 °K. Since that time many laboratories and scientists have been

investigating the mechanisms and structures of a wide variety of materials, looking for the next step towards room temperature superconductivity. Progress has been made, and useful systems which are superconductive at almost 100 °K have been devised. One of the most

promising material systems now being investigated is the yttrium-barium-copper-oxygen system. This system is being investigated as part of the NIST Superconductivity Program as well as in many other laboratories. As part of the NIST program, the Nuclear Methods Group was asked to provide analytical support for the materials research groups that were involved. This support involved both compositional analysis and stoichiometry analyses, and has been reported elsewhere [1].

It is reasonable to expect that trace element analyses may provide useful information in trying to understand the mechanisms and structure of high-temperature superconductors. It is still not clear what variables are important in making certain superconductors. The high temperature superconductivity must be demonstrated in a particular sample to know for sure that it will work. This report is on the analysis of starting materials supplied by three different materials research scientists at NIST, and included intermediates produced from some of these starting materials.

A total of 13 starting and intermediate materials were analyzed for up to 19 elements. Approximately 100 mg samples of each material were encapsulated in acid cleaned polyethylene vials and heat sealed. Standards used were monitor NAA constants normalized to iron foil fluence monitors, with small portions of multi-element Standard Reference Material 1633, Coal Fly Ash used as a control material to confirm the determined values. Samples and standards were irradiated for four hours in the NBSR RT-4 pneumatic tube irradiation facility at a reactor power of 19 MW and a neutron fluence rate of  $2.7 \times 10^{13} \text{ ncm}^{-2} \text{ s}^{-1}$ .

After irradiation, all samples and control materials were transferred out of the irradiated vials to standard counting dishes. Transferred sample weights were obtained and recorded. Samples were counted on a Gamma-X high purity germanium detector and associated pulse height analysis system, starting about 30 days after irradiation.

There were four groups of samples, from three different researchers. The most elements actually detected in any one sample was 13, and the average number of elements detected in each sample was eight. The elements determined and the ranges of impurity concentrations found in the superconductor starting materials were as follows: ytterbium,  $<0.01 - 1.1 \mu\text{g/g}$ ; selenium,  $<0.01 - 0.7 \mu\text{g/g}$ ; thorium,  $<0.003 - 0.7 \mu\text{g/g}$ ; chromium,  $<0.02 - 6.1 \mu\text{g/g}$ ; iridium,  $<0.02 - 6.2 \text{ ng/g}$ ; hafnium,  $<2 \text{ ng/g}$ ; barium,  $<2 - 320 \mu\text{g/g}$ ; strontium,  $<1 - 970 \mu\text{g/g}$ ; cesium,  $<0.001 - 2.0 \mu\text{g/g}$ ; terbium,  $<0.002 - 0.32 \mu\text{g/g}$ ; scandium,  $<0.05 - 37 \text{ ng/g}$ ; rubidium,  $<0.2 - 13 \mu\text{g/g}$ ; iron,  $<1 - 67 \mu\text{g/g}$ ; zinc,  $<0.05 - 410 \mu\text{g/g}$ ; tantalum,  $<3 - 42 \text{ ng/g}$ ; cobalt,  $<5 - 670 \text{ ng/g}$ ; silver,  $<0.01 - 2.9 \mu\text{g/g}$ ; europium,  $<0.5 - 1400 \text{ ng/g}$ ; antimony,  $0.02 - 14 \mu\text{g/g}$ . (NOTE: "less-than" values are the detection limits.)

The range of impurities of the various starting materials submitted was large. For example, four different copper oxides were analyzed, with total measured impurities ranging from  $2.51 \mu\text{g/g}$  to  $461 \mu\text{g/g}$ . The worst case was a yttrium-barium-copper intermediate, with almost  $1300 \mu\text{g/g}$  of measured impurities. On the other hand, one careful researcher worked only with highly purified materials, and all components were below  $3 \mu\text{g/g}$  total measured impurities.

In conclusion, INAA has been shown to be highly useful analytical technique for the measurement and evaluation of trace element impurities in many of the high temperature superconductor starting materials.

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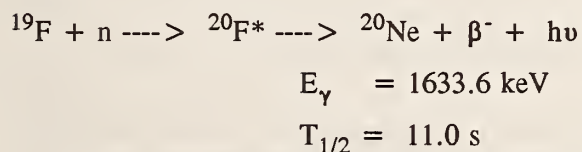
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# DETERMINATION OF FLUORINE IN VEGETATION REFERENCE MATERIALS BY INAA

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This project was undertaken to fulfill a need for an analytical method to determine fluorine in a variety of materials, but especially for the determination in biological and food SRMs. The ability to determine total fluorine in samples without losses due to dissolution is an important motivation for the development of such a procedure and INAA provides this. Further, a second method was needed (in addition to the ion selective electrode method) in order to certify fluorine in NIST reference materials.

To review the analysis system, the nuclear reaction to be used was:



The primary difficulty with this reaction is with the very short half-life of 11.0 s. This short half-life requires very fast transfer of the sample to the detector for reasonable sensitivity, plus it prevents the use of decay time as a method to eliminate or minimize interferences due to matrix radioactivity. Fortunately, the 1633 keV gamma ray has no significant interferences, the most important being the 1642.7 keV peak of chlorine which is well resolved from fluorine. There is a potential problem, due to the formation of  $^{20}\text{F}$  from sodium present in the matrix, via a (n, p) neutron reaction. This potential interference was investigated, even though it was felt that the very high ratio of thermal neutrons to fast neutrons of the RT-4 irradiation facility in the NBSR would minimize the importance of this interfering nuclear reaction. Other nuclear reactions that were considered for the determination of fluorine were fast neutron reactions producing fluorine-18 and oxygen-19. However, both of these reactions suffer from fatal flaws, and were deemed not acceptable.

The first requirement was to set up a detector and counting system close to the

irradiation facility in order to minimize the time between the end of irradiation and the beginning of the count. It was decided to use conventional electronics, rather than a newly developed "loss-free" counting system, which has yet to be made quantitative in our laboratory. In the author's experience, conventional electronics can be used without excessive errors as long as electronic dead times are kept below 40% and appropriate corrections are made.

After setting up, the system was evaluated using a piece of Teflon FEP as a fluorine standard. The amount of fluorine was calculated from the total weight based on the assumption that the Teflon was a  $[-\text{CF}_2-]$  polymer. The teflon was calculated to be 75.98% fluorine. Thus, a Teflon standard weighing 7.545 mg contained 5733  $\mu\text{g}$  of fluorine. A second standard of high purity calcium fluoride glass was also used. All samples and standards were encapsulated in polyethylene foil bags for irradiation and counting, and these bags were evaluated for fluorine content. The contribution of the sodium fast neutron interfering reaction was evaluated by irradiating samples of sodium chloride and sodium bicarbonate. Finally, a tentative procedure was evaluated by analyzing two reference materials, a high fluorine vegetation and a low fluorine vegetation. Six samples of each material were weighed into polyethylene foil bags and heat sealed. The sample weights varied from 198 mg to 332 mg, averaging approximately 270 mg. In addition, several other vegetation reference materials were also packaged for analysis.

A number of irradiation and counting combinations were tested and modified in order to obtain the optimum measurement characteristics for these vegetation samples. Even though the high fluorine vegetation has considerably more fluorine, the samples also had extremely high aluminum concentrations. Since the  $^{28}\text{Al}$  produced has a 2.3 m half-life, this interfered with the fluorine determination by producing a high matrix radioactivity and thus a

high counting deadtime. Eventually, optimum irradiation and counting procedures were developed for both of these materials.

The decay time required to remove the sample from the rabbit and then place it reproducibly on the detector ranged from 15 to 24 sec for the samples and standards. A measurement of the fluorine blank level of several empty polyethylene foil bags gave no measurable fluorine peak. In addition, several measurements of sodium compounds also yielded no measurable fluorine peak, even at a sodium concentration 30 times that expected in a 270 mg vegetation sample. In addition to the Teflon standard, a high purity  $\text{CaF}_2$  glass was obtained and used to confirm the reliability of the teflon as a fluorine standard. Both standards agreed well, to better than one percent.

Finally, samples of several vegetation materials were run using the developed

procedures. Both reference materials of primary interest had abnormally high aluminum contents as well as fluorine, a result of their being collected near an aluminum refining plant. The "low" fluorine vegetation was found to have  $78 \pm 12 \mu\text{g/g F}$ , while the "high" fluorine vegetation had  $440 \pm 58 \mu\text{g/g F}$  (1s). Both materials were near their detection limits, due to the high matrix activity, and were counted at 20 cm from the detector.

In conclusion, procedures have been developed for the determination of fluorine in the two types of vegetation reference materials. For the "low F" material, agreement with the previously determined values is good. For the "high F" material, these INAA results are substantially higher than values obtained using a dissolution method. Work is continuing to resolve this difference.

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## DETERMINATION OF LITHIUM IN GEOCHEMICAL REFERENCE MATERIALS BY THERMAL NEUTRON CAPTURE MASS SPECTROMETRY

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and

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Thirteen geochemical reference standards have been analyzed for lithium by a technique originally developed for biological materials [1]. The technique consists of thermal neutron irradiation, then mass spectroscopy measurement of  $^3\text{He}$ . During thermal neutron irradiation of the samples, tritons are produced mainly by the reaction  $^6\text{Li}(n, \alpha)^3\text{H}$  with the remainder from  $^2\text{H}(n, \gamma)^3\text{H}$ . The 2.73 MeV tritons from  $^6\text{Li}$  are stopped either in the sample, or in the polyethylene liner wall.  $^3\text{He}$  from decay of  $^3\text{H}$  (half-life = 12.38 y) escapes rapidly to the gas phase inside the evacuated lead irradiation capsule and, after a suitable waiting time, can be measured by high-sensitivity mass spectrometry.

Early tests of this method carried out with 0.1-0.4 g samples of finely ground clay and other geological materials showed that about 50% of the  $^3\text{He}$  was retained by the mineral even when samples were heated to 250 °C over

the decay time. To ensure complete release of  $^3\text{He}$ , temperatures above 1200 °C would probably be required. To avoid such difficulties 5-10 mg of the reference materials were ground with acetone in a small agate mortar to a particle size of 1-5  $\mu\text{m}$ , a thickness less than the range of the tritons in the geological materials (20-40  $\mu\text{m}$ ). The materials were then dispersed upon a polyethylene (abbreviated PE) disk and after all the acetone had evaporated, the sample was covered with a second PE disk and sandwiched between two pieces of glass in a small vacuum apparatus. Each layer of PE is thicker than the range of the tritons in PE, i.e. 59  $\mu\text{m}$  [3]. The apparatus was placed on a hot plate at about 150 °C, until the PE disks had melted. Although this modification requires a small sample size,  $\approx 15$  mg, the sensitivity for  $^3\text{He}$  is such that lithium concentrations of about 0.1 ppm by weight can easily be measured.

Several types of blank samples were prepared: 1) PE disks were cleaned by washing in dilute  $\text{HNO}_3$ , distilled water, and acetone, then weighed and transferred to lead irradiation tubes. 2) Disks were prepared as above and melted in the vacuum apparatus before transferring to irradiation tubes. 3) Disks were prepared as in 2) except that the PE was placed in a pyrex cylinder, 2 ml of acetone was added, and then the assembly was treated in the same way as for reference materials. 4) About 5 mg of spectrosil<sup>tm</sup> fused quartz ( $\text{Li} = 1.8 \pm 0.1$  ppb) was ground in the mortar and then the procedure used for the reference materials was followed.

A standard solution containing 231.2 ppb Li was prepared by dissolving an accurately weighed amount of  $\text{Li}_2\text{CO}_3$  in distilled water. A single drop of the standard solution (about 20 mg) was placed on a preweighed PE disk while it was on the balance pan; the disk plus drop was weighed immediately, then freeze-dried to remove water. Tests showed that there was negligible weight loss of the drop during weighing. Finally, the dry sample was sandwiched against another PE disk in the vacuum apparatus.

The PE-encapsulated samples were folded with tweezers and placed in pure lead tubes (o.d. = 0.64 cm, wall thickness = 0.16 cm) which were pinch-sealed at one end. The lead tubes were attached with clamps to a stainless steel manifold on a vacuum line to completely remove atmospheric He dissolved in the PE, then pinch-sealed to form a rugged container for neutron irradiation.

The irradiations were carried out in the thermal column for a highly thermalized neutron fluence rate of about  $3.6 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ . Sixteen lead tubes were placed in each "rabbit" (a total of 10-12 samples of reference materials, at least 2 Li standards, and at least 2 blanks). Irradiation times were from 48 h to 96 h.

Although a waiting period of a few days would have sufficed to ensure adequate amounts of  $^3\text{He}$ , the actual waiting period was from 3-6 months. The lead tubes were placed in a mass

spectrometer inlet system and punctured with a pin attached to a bellows. The released gas was purified through activated charcoal at 186 °C and admitted to the mass spectrometer.  $^3\text{He}$  and  $^4\text{He}$  ion currents were recorded. Analyses of samples were interspersed with analyses under identical instrumental conditions of samples of a helium standard and with inlet system blanks [5]. The detection limit of the mass spectrometer for  $^3\text{He}$  is about  $2 \times 10^4$  atoms. This is equivalent to  $1.3 \times 10^{-11} \text{ g Li}$ , or a concentration of 2.7 ppb in a 5 mg sample assuming a neutron fluence rate of  $3.6 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ , and irradiation time of 24 h, and a cooling time of 1 month.

Analyses of the "blank" pieces of PE showed that there was some lithium in which the results fell in two distinct groups,  $4.7 \pm 0.4 \text{ ng/g}$  ( $n = 6$ ) and  $20.1 \pm 1.1 \text{ ng/g}$  ( $n = 11$ ). This can be explained by the fact that the disks were cut from two different PE bags. Two disks weigh about 35 mg, thus the actual lithium blanks were about 0.16 ng and 0.70 ng. Most of the error in the concentration is due to the uncertainty in the sample mass. No other difference between blanks prepared in different ways were noted.

There are only two other known reactions apart from  $^6\text{Li}(n,\gamma)^3\text{H}$  which produce  $^3\text{H}$  in a highly thermalized neutron flux:  $^2\text{H}(n,\gamma)^3\text{H}$ , and ternary fission of  $^{235}\text{U}$  which produces a very small amount of  $^3\text{H}$  [6]. The worst case sample was PCC-1 No. 2, where the correction is only 3.3% of the observed  $^3\text{He}$ .

The results are given in table 1 along with literature values for comparison. The agreement appears to be quite good for concentrations above about 30 ppm, but for lower concentrations, our results, with the exceptions of PCC-1, appear to be significantly lower than the literature values. The results presented show that the  $^3\text{He}$  technique is applicable to geochemical materials. The method has two main advantages: it is remarkably free of interferences or matrix effects, and does not require dissolution of samples which should result in lower blank levels than some other methods.

## NUCLEAR ANALYTICAL CHEMISTRY

**Table 1.** Lithium concentrations in ppm for some geochemical reference materials. Column 3 gives numbers of separate samples determined by the  $^3\text{He}$  method. Errors are estimates of random and systematic components at one standard deviation, including sample inhomogeneity. Column 5 gives recommended and proposed values taken from Govindaraju [2]

Agency	Material	n	$^3\text{He}$ Method	Values
USGS	AGV-1	4	$9.5 \pm 0.4$	<u>12</u>
	BCR-1	3	$12.0 \pm 0.7$	<u>12.9</u>
	DTS-1	3	$1.36 \pm 0.08$	<u>2.1</u>
	G-2	3	$29.7 \pm 2.0$	<u>34</u>
	GSP-1	4	$30.2 \pm 1.3$	<u>31</u>
	PCC-1	4	$0.87 \pm 0.06$	1.6
CCRMP	MRG-1	3	$3.10 \pm 0.18$	4.2
	SY-3	2	$90. \pm 7$	<u>92</u>
NRC	BCSS-1	4	$41.4 \pm 2.8$	
	MESS-1	3	$35.6 \pm 2.7$	
ZGI	BM	3	$79. \pm 7$	<u>72</u>
	TB	3	$111. \pm 10$	<u>111</u>
NIM	S	3	$0.94 \pm 0.05$	2

We wish to thank W. C. Eismont and R. M. Clarke for assistance with the mass spectrometer work, O. Mudroch who donated geochemical reference materials, and the operations staff at the NIST reactor for their cooperation. This work was supported in part by a grant from the Natural Sciences and Engineering Research Council of Canada.

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## BULK LITHIUM CONCENTRATION BY THERMAL NEUTRON TRANSMISSION

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and

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The National Institute for Standards and Technology (NIST) and Westinghouse Savannah River Site (SRS) have collaborated in a determination of the  $^6\text{Li}$  content of lithium-aluminum alloy tubes. The method employed for the Li determination was the measurement of thermal neutron transmission. Four different fabrication styles of tubes were measured. Since the neutron beam only sampled a small volume of the tube, the tubes were rotated during the measurement to average over all azimuthal angles. Blanks (tubes without lithium) were provided for all but one of the series. For these, the tube ends which do not contain lithium were used as blanks. Since the original tube lengths of about 4.5 m were too long to be handled in the limited space available at the thermal column, the tubes were quartered (by SRS) and

the transmissions of each section measured separately. The data for the separate pieces was then combined for the final analysis. To demonstrate the ability of the transmission method to accurately determine lithium content, two LiF single crystals (natural lithium) were purchased to be used as "standards". These were 30.00 mm diam disks, approximately 1 mm thick. This thickness was chosen since by measuring either one or both disks, the transmission would be approximately the same as the unknowns. The masses of the disks were determined by "weighing", after which small scrapings were sent for mass spectroscopic analysis to determine the  $^6\text{Li}/^7\text{Li}$  ratio. The purpose of the standards was to demonstrate our ability to accurately measure the transmission of samples whose transmission could be readily

calculated. It was never intended to use the LiF results to renormalize the data of the tubes.

**Experimental Procedure**--All transmission measurements were made using the central beam port of the graphite thermal pile of the NIST reactor. A 14 mm diam aperture was placed at the outer edge of the thermal pile and a 13 mm diam aperture placed at the edge of the biological shield. The distance between these two apertures was 788 mm, giving an angular divergence of less than 2 degrees. A fission chamber was placed at the exit aperture to serve as a run-to-run monitor. The samples (in their rotator-translator) were 244 mm from the exit aperture. A second fission chamber, the transmission detector, was a distance of 622 mm from the exit aperture. All of the components were aligned optically to an accuracy of about 0.5 mm. All of the data was taken with an 80386 computer which also automatically moved the sample at the end of each data taking interval. Preliminary data processing was also done by this computer at the end of each interval.

The routine was to systematically measure each series and also to periodically measure the LiF transmissions. The LiF transmissions were measured four different ways. For each of the three blanks, a small slot was cut to hold the LiF piece in the center of the tube. The transmission was measured by cycling the LiF in and out of the beam, i.e., by translating the tube by 10 cm and then back. Additionally, the LiF was also mounted free-standing in air and cycled in and out of the beam. In all configurations, the transmission of one piece of LiF (#1) and both pieces of LiF (designated B) were measured.

**Results**--Lithium Fluoride "Standards". Using the isotopic ratio obtained from the mass

spectroscopic analysis, and ENDF/B-V values for the cross sections, a calculated value was obtained for the transmission of both the single and double thick LiF crystals. The Maxwellian temperature chosen for the neutron energy distribution was 324 K which is equivalent to a neutron energy of 27.9 meV. This value was based on previous measurements of the neutron distribution made with a chopper. The statistical uncertainty of the measured value is  $\pm 0.1\%$ . For the calculated value, there are two sources of uncertainty, the isotopic enrichment and the temperature of the Maxwellian spectrum. The uncertainty of the isotopic enrichment was  $\pm 0.2\%$ . This contributes  $\pm 0.1\%$  to the uncertainty in the transmission of the single crystal (LiF1) and  $\pm 0.2\%$  to the uncertainty of the double thick crystal (LiFB). The uncertainty of the Maxwellian temperature was estimated to be  $\pm 5$  K, this adds an uncertainty of  $\pm 0.4\%$  and  $\pm 0.7\%$  to the uncertainties of LiF1 and LiFB, respectively. The ratio of the measured to the calculated transmissions is  $.993 \pm .005$  for LiF1 and  $1.002 \pm .008$  for LiFB. The final one-sigma ( $1\sigma$ ) uncertainties were obtained by adding the individual uncertainties in quadrature. In comparing measured to calculated concentrations, as opposed to transmissions, the ratio of measured to calculated is  $1.014 \pm .010$  for LiF1 and  $.998 \pm .008$  for LiFB.

**Alloy tubes.** The alloy tube data was analyzed in a similar fashion, with the additional complication of the cylindrical geometry. The final one-sigma uncertainties ranged from  $\pm 0.8\%$  to  $\pm 2.8\%$  (for the thinnest samples). The uncertainty in the thicknesses of the blanks dominate the uncertainty for the thinnest samples.

**INCLUSION OF MARINE MAMMAL TISSUES IN THE  
NATIONAL BIOMONITORING SPECIMEN BANK**

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Due to increasing interest and concern about the effects of environmental contaminants on various marine mammals in the United States and many other parts of the world, the National Biomonitoring Specimen Bank (NBSB) has been used for several projects in collaboration with two branches of the National Oceanic and Atmospheric Administration (NOAA). The NBSB, located in the reactor building at NIST, is the repository for carefully collected and preserved samples that are representative of the environment at the time of collection [1]. Subsamples of selected specimens are analyzed at the time of collection for pollution monitoring, and the remainder is banked for future analyses. The majority of the inorganic analyses is accomplished using the NBSR to perform neutron activation analysis (NAA), a non-destructive multi-element technique [2,3].

In 1987, NOAA and the Minerals Management Service initiated a project for the archiving of tissues from selected Alaskan marine mammals (the Alaskan Marine Mammal Tissue Archive Project, or AMMTAP). Many of the native Alaskans still rely on marine mammals for subsistence. Due to the modern industrial expansion in petroleum exploration and mineral mining, environmental monitoring of marine mammals in these areas is advantageous both for the population for whom this is a food source and for assessing the environmental impact of these anthropogenic activities. Logistics and protocol development for sampling were a challenge due to the Alaskan environment. Protocols were developed for the collection of tissues from animals taken by natives during subsistence hunting [4].

Two documents describing the AMMTAP program are nearing completion. The first describes the revisions in the sample collection

protocol that were developed as more field experience was obtained. The second is a comprehensive description of the five year project and includes the sample inventory and results from organic and inorganic analyses (see table 1). Baseline data have been gathered from approximately 20% of the collected tissues. The tissues are analyzed for trace elements and for selected organic contaminants. Trace element analyses were performed using NAA to determine concentrations for about 36 elements. These results provide a unique and extensive data base for elemental concentrations in marine mammal tissues, since other works have generally reported concentrations for only five to ten elements.

In 1990, NOAA and the National Marine Fisheries Service initiated a similar project, the National Marine Mammal Tissue Bank (NMMTB), for the analysis and archival of tissues from marine mammal species found in the United States (excluding Alaska). This project began as a pilot program for sampling tissues from animals in the northeast region, and has been conducted in cooperation with the New England Aquarium and the Marine Mammal Stranding Network. Two sampling protocols were developed: (1) for animals from incidental catches by fishing vessels and (2) for animals from mass strandings. Both protocols were implemented in the collection of liver and blubber tissues from ten animals. A portion of the samples were prepared for NAA of trace elements and for chromatographic measurements of selected organic compounds (chlorinated pesticides and polychlorinated biphenyls). This pilot program has been very successful and there are now plans to extend the program to include samples from the southeast and Gulf coastal areas and, eventually, from the west coast.

## NUCLEAR ANALYTICAL CHEMISTRY

**Table 1.** Inventory of marine mammal specimens in the National Biomonitoring Specimen Bank

Program	Species	Number of animals <sup>a</sup>
	Northern Fur Seal	15
Alaska Marine	Ringed Seal	28
Mammal	Bearded Seal	3
Tissue Archive	Harbor Seal	3
	Spotted Seal	1
(NOAA/MMS)	Stellar Sea Lion	1
	Belukha Whale	14
National Marine	Harbor Porpoise	5
Mammal Tissue Bank (NOAA/NMFS)	Pilot Whale	5

<sup>a</sup>Samples of blubber, liver and kidney are collected from each animal in the AMMTAP; samples of blubber and liver are collected from each animal in the NMMTB.

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## BORON AND LITHIUM IN TOTAL MIXED DIETS OF COUNTRIES PARTICIPATING IN THE IAEA PROJECT ON DIETARY INTAKE OF MINOR AND TRACE ELEMENTS

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A coordinated research program initiated by the International Atomic Energy Agency (IAEA Vienna, Austria) in 1985, and supported by the Food and Drug Administration (FDA), the National Institute of Standards and Technology (NIST) and the U.S. Department of Agriculture (USDA), is currently under way. The purpose of this project is to obtain reliable comparable data on the average daily intakes of nutritionally important minor and trace elements from diets consumed in a number of developed and developing countries such as Australia, Brazil, Canada, China, Iran, Italy, Spain, Sudan, Sweden, Thailand, Turkey, and the United States. The program is due to be completed in 1991, by which time approximately 450 diets will have been analyzed. The analytes of interest include practically all the minor and trace elements considered to be of biological interest. In view of the emerging interest in boron and lithium in animal and human

nutrition, analytical work was extended to include these two elements. As a first step, diets from China, Italy, Spain, Turkey, and the United States have been analyzed. Boron and Li in mixed total human diets were determined by the method of neutron activation-mass spectrometry (NA-MS). The origin of this technique [1] and its application to a wide variety of biomatrices [2] have been previously described.

The food composites from the United States represent FDA's Total Diet Study, and reflect the daily consumption of foods by 25 to 30-year-old males. Presently, five of the ten collections from different regions of the country have been analyzed. The average daily intake amounts to  $1.5 \pm 0.25$  (range 1.3-1.8) mg of B, and  $37.35 \pm 14.6$  (range 25-62)  $\mu\text{g}$  of Li. For other countries, presently diets from Spain ( $n = 20$ ), Italy ( $n = 15$ ), and Turkey ( $n = 6$ ) have been analyzed and show the following results:

for Li ( $\mu\text{g/d}$ ) -

Spain  $53.5 \pm 25.3$  (range 10.9-104.7),  
Italy  $27.8 \pm 8.2$  (range 16.2-44.6), and  
Turkey  $39.3 \pm 10.3$  (range 29.3-50.9); and

for B ( $\text{mg/d}$ ) -

Spain  $2.16 \pm 0.97$  (range 0.69-4.12),  
Italy  $3.67 \pm 1.05$  (range 2.11-5.76), and  
Turkey  $1.41 \pm 0.34$  (range 1-1.9).

Additional diets from these countries are being analyzed to examine the differences in intake, if any, between rural and urban eating habits. The daily intake of Li calculated from the present study is lower than indicated in earlier published studies, and similar to the trend observed for B.

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## DIETARY INTAKE OF MINOR AND TRACE ELEMENTS IN THE UNITED STATES

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A coordinated research program on Human Daily Dietary Intakes of Nutritionally Important Trace Elements as measured by Nuclear and other techniques, initiated by the International Atomic Energy Agency (IAEA), is currently under way. Briefly, the purpose of this program is to obtain reliable analytical data on the average daily intakes of several important macro and trace elements in diets consumed in a number of developed and developing countries. The experimental approach consists of collecting total mixed diets or duplicate diets from the participating countries for the determination of nutrient elements such as Ca, Mg, Cu, Fe, I, Se, and Zn, as well as the toxicants Al, As, Cd, Hg, and Pb in view of their biological significance in the diet. The U.S. participation in this program involves laboratories from three governmental agencies: the National Institute of Standards and Technology (NIST), the Food and Drug Administration (FDA), and the U.S. Department of Agriculture (USDA).

The analytical data obtained for the U.S. diet composites are part of the IAEA study mentioned above. The participating countries are Australia, Brazil, Canada, China, Iran, Italy, Spain, Sudan, Sweden, Thailand, Turkey, and the United States of America, and the work is still in progress [1].

The Total Diet Study (TDS) developed by the FDA (2) has been used as the source to obtain foods for preparing U.S. diet composites. The quantity of foods consumed by the 25-30-year old male, the highest intake group in the TDS scheme, has been used as the basis for preparing the total mixed diet composites. Foods in the TDS are collected regionally four times a year by FDA's field personnel, shipped to the FDA Kansas City laboratory where they are prepared as ready-to-eat-foods and analyzed. Portions of prepared foods were packed in routinely used domestic quality ziplock type plastic bags, identified by a tag, frozen, and shipped by air in batches under dry ice packing to the Nuclear Methods Group laboratory for further processing. The total mixed diet composites were prepared by pooling appropriate quantities of the 201 food items as described in the TDS study. The elemental analysis was carried out mainly by instrumental and radiochemical neutron activation analysis (INAA and RNAA). The inorganic constituents determined are macro elements Ca, Cl, K, Mg, Na, and P, and trace elements Al, As, Au, Br, Cd, Co, Cr, Cs, Cu, Fe, Hg, I, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Se, Sn, Sr, V, Zn, and W. Elements that could not be determined by NAA

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were assayed by other methods under collaboration as described [1].

The results are compared with the daily intakes of the same age group published by the FDA-TDS scheme (table 1) which is based on individual analysis of the 201 food items [2,3]. In the TDS scheme, about 8 to 10 aliquots from each of the 201 different foods are individually analyzed for several elements. Concentrations are tabulated and stored in a computer. By using these values, the daily intake of a given element is computed by taking appropriate proportions of the 201 foods that were required to make up a day's diet [2] for the age-sex group in question. In contrast to several hundred separate foods analyzed in the TDS scheme, the results for USDIETS are obtained by analyzing a small number of test portions of the total diet composites. As shown in table 1, there is very good agreement between USDIETS and FDA-TDS investigations for the daily intakes of Ca, K, Mg, Na, and P. Cl was not determined in the TDS study. The daily intakes calculated for the essential trace elements also agree well with the FDA-TDS results as well as with the

prevalent dietary recommendations [4] as shown in table 1. However, the daily intake for iodine obtained through USDIET composites is about 70% of that of TDS. It should be noted that the TDS results shown in table 1 are for the years 1982-1989, while the USDIET composites cover the years 1985-1987. Therefore, the differences seen in the intake of iodine may reflect variations in iodine content of the foods collected during those years. The daily intake for the toxic elements As, Cd, Hg, and Pb obtained by the mixed total diet composite approach also agrees with the TDS estimates and are well below the tolerance limits suggested by nutritional authorities [5]. For several additional elements such as Au, Br, Cr, Cs, Rb, Sb, Sc, and Sn, the daily intake data could be obtained by USDIET composites.

The results from this study have demonstrated that analysis of mixed total diet composites can be a valuable supplement to the data obtained by the TDS scheme. The comparison shows that for 20 elements which have been investigated by both approaches, the results agree well.

**Table 1.** Comparison of the daily intakes of various minerals from USDIET composites and FDA-TDS based on a daily intake of 3075 g of food applicable to male, 25-30-year old age group (1-3)

Element	Unit	DAILY INTAKE		
		USDIETS <sup>a</sup> (Composites)	FDA-TDS <sup>b</sup>	RDA-ESADDI or PTDI <sup>c</sup>
Ca	mg	860±150	858	800
Cl		3950±103	-	1700-5100
K		2800±88	2998	1875-5625
Mg		275±11	301	350
Na		2820±130	3040	1100-3300
P		1520±61	1528	800
Co	µg	14±2	11	0.12
Fe		<39±7 <sup>d</sup>	-	50-200
Ce		1320±170	1220	1500-3000
Fe		14350±1070	16200	10000
I		280±87 <sup>e</sup>	410	150
Mn		2490±207	2810	2000-5000
Mo		125±7	116.5	75-250

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Ni		190±38	146	-
Se		110±8	110	70
Zn		16000±1010	16400	15000
V		16±3	18	-
Al		11800±2230	13660 <sup>f</sup>	60000
As		47±8	45	120
Cd		13±2	15	60-72
Hg		3±1	4	42
Pb		34±18	41	430
Au		0.7±0.5		
Br		4680±800		
Cs		9±1		
Rb		2440±450		
Sb		4.0±0.5		
Sc		0.40±0.04		
Sn		3200±450		
Sr		1620±240	1490	
W		4.0±1.2		

<sup>a</sup>Calculated from the average concentrations of diet composites representing collections between 1985-87.

<sup>b</sup>FDA-TDS results for Na, K, Ca, P, Mg, Fe, Zn, Se, I, Cu, and Mn are for all collections between 1982-89. Others are for all collections between 1982-86.

<sup>c</sup>Recommended Dietary Allowances (single values) or Estimated Safe and Adequate Daily Dietary Intakes (ranges) (4). PTDI applies to Al, As, Cd, Hg, Sn, and Pb taken from sources listed in Reference 5.

<sup>d</sup>See discussion.

<sup>e</sup>Reference 6 for USDIETS I-V analyzed for the IAEA project.

<sup>f</sup>From one collection in 1984.

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### NEUTRON ACTIVATION ANALYSIS AT THE FOOD AND DRUG ADMINISTRATION

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The Food and Drug Administration (FDA) maintains a neutron activation analysis (NAA) facility in the reactor building of the National Institute of Standards and Technology (NIST). This facility is directed by FDA's Center for Food Safety and Applied Nutrition and provides agencywide analytical support for special investigations and applications research. NAA complements other analytical techniques used at FDA and serves as a reference technique and confirmatory quality assurance (QA) tool. Instrumental, neutron-capture prompt- $\gamma$ , and radiochemical NAA procedures (INAA, PGAA, and RNAA, respectively) continue as the prime nuclear analytical approaches. A radioisotope-induced X-ray emission (RIXE) spectrometer provides support for FDA programs which monitor toxic elements in housewares (especially Pb), and the low-level  $\gamma$ -ray counting facility developed by the Nuclear Methods Group of the NIST Center for Analytical Chemistry is used to determine the radionuclide content in various matrices. This combination of analytical techniques enables diverse multielement and radiological information to be obtained for foods and related materials.

FDA's NAA laboratory served as the reference laboratory in a QA exercise that involved several of FDA's major analytical centers. Two well-characterized biological materials were distributed for multielement analysis and the results were tabulated at the NAA laboratory. The findings, which will be summarized and distributed to participating laboratories, will be used by the laboratories as a basis for procedural reviews and as a guideline to further improve accuracy and precision.

There is a need in the analytical community for infant formula reference materials (RMs). A preliminary investigation of powdered infant formula showed that this material had favorable moisture pickup and homogeneity characteristics, indicating that the matrix is a good candidate RM. As the 1990-1991 year

closes, a multiagency joint effort is now under way to develop a large batch of powdered infant formula as an RM. FDA, the U.S. Department of Agriculture, and NIST are combining their efforts to make this material available with both element concentration and organic nutrient concentration information. Pre-release analytical work is expected to begin next year.

Thermal neutron PGAA research concentrated on optimizing the technique for the analysis of food. Improvements in the Compton suppression electronics and alignment procedures have lowered backgrounds significantly. H and B backgrounds were lowered by more than a factor of two, and the Compton background was lowered by a factor of three. A systematic study of backgrounds and their enhancements due to neutron scattering resulted in a significant reduction of analytical uncertainty introduced by background correction.

A collection of 234 Total Diet Study foods is being analyzed by PGAA. Unlike most previous studies, these foods are being analyzed without prior drying to eliminate the possibility of element losses, especially those of B. Duplicate portions of about 40 foods have been analyzed for H, B, Na, Cl, S, K, Ca, and Cd. The system improvements discussed above allowed use of larger test portion sizes and enabled count times to be shortened by about a factor of 10 while comparable detection limits were maintained. Current detection limits (15- to 20-h counts) for 2-g food test portions are given in table 1. Detection limits for elements other than H and Cl are about a factor of 3 greater when Cl is present at levels  $\geq 1\%$ . Findings from this study will be presented at the 8th International Conference, Modern Trends in Activation Analysis (MTAA8) in Vienna, Austria, in September 1991, and published in the Journal of Nuclear and Radioanalytical Chemistry [1]. Two other PGAA articles [2,3] dealing with food analysis were published during the past year.

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Studies continued on PGAA matrix effects associated with thermal neutron scattering [4]. The effects cause enhancements of element sensitivities and background count rates. This work and its relevance to analysis of food and biological material will be presented in two papers [5,6] at MTAA8.

**Table 1.** Analytical  $\gamma$ -rays, detection limits and interferences for food analysis by PGAA. "Bkg" denotes interferences due to activation of apparatus and shielding.

Element	keV	DL ( $\mu\text{g/g}$ )	Interferences
H	2223	36	bkg
B	477	0.04	Na, Cl, bkg
Na	472	69	bkg
Cl	787	7	bkg
S	841	155	K
K	770	65	-
Ca	6420	330	bkg
Cd	558	0.05	-

DL = detection limit.

The first cold neutron PGAA beam was extracted at the NIST Cold Neutron Research Facility on October 29, 1990. The cold neutron fluence rate was  $\sim 1.4 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$  (thermal equivalent). Compared with the current thermal-neutron PGAA system, there were improved element sensitivities as a result of a much more favorable detector-to-sample geometry. Signal-to-noise ratios were significantly better because the cold neutron beam lacks the  $\gamma$ -ray component found in the thermal neutron beam. Measured sensitivities (counts  $\text{s}^{-1} \text{ mg}^{-1}$ ) for Standard Reference Material 1566, Oyster Tissue, were better than thermal PGAA by a factor of  $\sim 6$  for H, B, K, Cl, and S and a factor of  $\sim 3$  for Cd. Detection limits would be lowered by a factor of 2-3 if low backgrounds (comparable to or better than those for the thermal facility) can be achieved. Future improvements, e.g., the addition of a bismuth germanate scintillation detector for Compton suppression and installation of the new cold source, will also help reduce the detection limits. The status of cold neutron PGAA will be presented in a paper at MTAA8 [7].

RIXE experiments were conducted to study the glazes of 10 ceramicware items collected in the People's Republic of China. By using a  $^{109}\text{Cd}$  excitation source, Pb was detected in four items. Other elements observed included Au, Fe, Nb, Y, Zn, and Zr. More than 100 ceramic test tiles with a wide range of glazes are being analyzed by  $^{109}\text{Cd}$  RIXE.

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ATMOSPHERIC AND ENVIRONMENTAL STUDIES BY INSTRUMENTAL AND NEUTRON-CAPTURE PROMPT  $\gamma$ -RAY ACTIVATION ANALYSIS

G. E. Gordon, J. M. Ondov, and W. B. Walters (University of Maryland, College Park, MD)

Now that the reactor is again operating on a fairly routine schedule, we are making extensive use of it. We completed a study of the effects of target shape and neutron scattering by hydrogen on sensitivities for various elements by neutron-capture prompt  $\gamma$ -ray activation analysis (PGAA), as discussed by Mackey et

al. in the following section. This work is being done in preparation for the use of cold neutrons in PGAA. Also, we briefly note projects in which we have collected large numbers of samples of airborne particles, which are being irradiated now.

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EFFECTS OF TARGET SHAPE AND NEUTRON SCATTERING BY HYDROGEN ON NEUTRON-CAPTURE PROMPT  $\gamma$ -RAY ACTIVATION ANALYSIS (PGAA)

E. A. Mackey and G. E. Gordon (University of Maryland, College Park, MD)  
and

R. M. Lindstrom (Center for Analytical Chemistry)

We have studied the effects of neutron scattering by H on analytical sensitivities (cps/mg) of neutron capture prompt  $\gamma$ -ray activation analysis (PGAA). Hydrogen causes a particular problem because of its large free-atom scattering cross-section,  $\sigma_{\text{scat}} = 20.5$  b. For eleven elements in liquid matrices of constant shape, sensitivities increase linearly with increasing H concentration over the range of 0 to 11% H. Also, for hydrogenous samples, sensitivities vary with sample shape [1]. The magnitude of these effects can be as large as 25%. Because both sample shape and the amount of H affect sensitivities, further studies were performed to determine a method of analysis which would allow accurate data interpretation with minimum uncertainty.

In work now published [1], we found that sensitivities for various elements in hydrogenous materials in disks, 12.7-mm diam, increased with disk thickness up to about 2 mm and then decreased with further increasing thickness. At thicknesses approaching the disk diameter, sensitivities were approximately the same as those of non-hydrogenous samples, suggesting that, as the samples approach a spherical shape, the scattering effects cancel out. This was

confirmed by the analysis of H in spheres and disks of paraffin (the former being cast in bullet molds). As we reported in last year's progress report, we confirmed the paraffin results for other elements in other materials by irradiating samples formed with a die for making spherical samples of urea, tris-(hydroxymethyl)-aminomethane (THAM), paraffin, SRM 371g Sulfur; and SRM 1632a Bituminous Coal.

During the past year we analyzed solutions containing known amounts of individual elements. The solutions were placed in a series of spherical quartz globes (made by Jeff Anderson of the NIST glass shop) of internal diameters ranging from 5.4 to 11.7 mm. In addition, as we had done previously for solutions contained in Teflon bags, we kept size constant while varying the H concentration by use of three types of solution: pure D<sub>2</sub>O (0% H), 50% H<sub>2</sub>O/50% D<sub>2</sub>O (5.6% H) and pure H<sub>2</sub>O (11.2% H).

Results from these experiments are summarized in table 1. Each entry in the central three columns represents the average of sensitivities measured in up to six spherical globes of different diameters. The fact that the relative standard deviations of these values is

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quite small means that the sensitivity is independent of size for these spherical samples, as expected from the theoretical treatments. Also, except for Gd, the sensitivities for each element are the same, within uncertainties, for solutions containing different amounts of H and for non-hydrogenous standards. However, there are problems for the Gd solution and for more concentrated Sm solutions. Note in table 1 that the sensitivity for Gd in pure H<sub>2</sub>O is significantly greater than for the other solutions. Furthermore, when we use a more concentrated Sm solution (1.96 mg/mL vs. 0.56 mg/mL for table 1), the sensitivity for Sm determinations increases with volume of the spherical globes, as shown in figure 1. In addition, the sensitivity for the detection of H itself in the H<sub>2</sub>O of the Sm solutions increases by about the same factor.

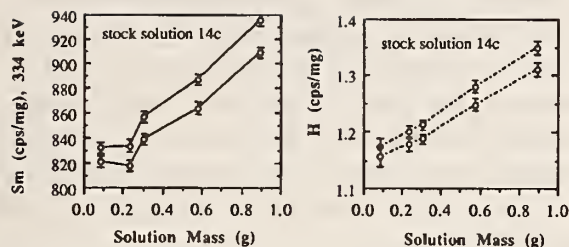
Both Gd and Sm possess isotopes for which the absorption cross-section curves include very strong low energy neutron-capture resonances.

A resonance might increase the effective absorption cross section for that element, causing more self shielding, or cause spectral hardening. However, any of these effects would result in a *decrease* in the fluence rate within the sample. No enhancements were observed for the "1/v" nuclides. We know of no mechanism by which the presence of isotopes possessing absorption resonances might *increase* sensitivities.

Many of the enhanced sensitivity effects in non-spherical targets reported here and our previous study [1] can be understood, at least qualitatively, in terms of isotropic, elastic neutron scattering [2-4]. However, it does not appear possible for that simple approach to account for several observations:

- (1) enhancements for H itself and for Sm that are significantly smaller and for Mn greater than those for other elements and
- (2) several unusual behaviors of solutions containing Gd and Sm.

Table 1. Element sensitivities measured in aqueous solutions contained in quartz globes				
Element	element sensitivity in :			standards
E <sub>γ</sub> (keV)	H <sub>2</sub> O	50% H <sub>2</sub> O	D <sub>2</sub> O	(0% H)
B (447)	730 ± 9	732 ± 9	715 ± 9	703 ± 4
Br (245)	0.298 ± 0.007	---	---	0.308 ± 0.005
Cd (558)	219 ± 3	212 ± 2.4	211 ± 3	---
Cl (516)	2.30 ± 0.03	2.24 ± 0.02	2.23 ± 0.03	1.21 ± 0.01
Cl (787)	1.94 ± 0.04	1.91 ± 0.01	1.90 ± 0.03	2.22 ± 0.08
Gd (182)	1034 ± 17	960 ± 14	948 ± 8	---
H (2223)	1.24 ± 0.01	1.18 ± 0.02	---	---
K (770)	0.195 ± .010	---	---	0.199 ± 0.013
Sm (334)	851 ± 4	860 ± 6	---	---
Sm (439)	417 ± 4	422 ± 5	---	---



**Figure 1.** Samarium (a) and H(b) sensitivities measured in stock solution 14c. The upper curve represents data that were corrected for self-absorption and the lower, data that were not corrected.

As discussed above, the unusual results for Sm and Gd suggest a possible role of low energy neutron resonances, which are quite strong in both elements, but the most obvious explanations work in the opposite direction from the observations. It will probably be necessary to include effects of energy-dependent cross sections and changes in neutron energy spectra within samples to achieve a full understanding of the observations.

A paper covering the new results from this project is being prepared for submission to *Anal. Chem.* [5].

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## SUBMICROMETER SIZE DISTRIBUTIONS OF AIRBORNE PARTICLES BEARING VARIOUS TRACE ELEMENTS

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Knowledge of the composition and size distributions of atmospheric fine particles is important because these parameters govern respirability, deposition, nucleation of water vapor and light scattering. Submicrometer particles are of special interest, as they are respirable, have long atmospheric residence times, and are frequently enriched in potentially toxic species. Trace elements borne by these particles are also useful for apportioning sources and tracking air masses over long distances. Despite the importance of this information, reliable measurements of the distributions of major, minor and trace constituents of the submicrometer aerosol have been limited because of limitations of the equipment available for reliable collection and analysis of particles in size cuts ranging far below 1- $\mu$ m diam. As described in last years' Progress Report, in

1981, Kuhlmeier et al. developed an impactor capable of sizing submicrometer particles at modest pressure drops (i.e., about 250 torr for 0.06- $\mu$ m minimum size cut) and modest jet velocities (127 m/sec for 0.09- $\mu$ m cut) using micro-orifice technology [1]. The impactor's low pressure drop and 28-L/min flow rate permit collection of samples suitable for trace analysis with a standard air-sampling pump.

In work now published, we tested the micro-orifice impactor (MOI) by collecting particles at a rural site in western Maryland near Deep Creek Lake [2]. Most samples were collected between 1 and 31 Aug., 1983, with sampling periods ranging from 6 to 24 hr. Cutoff diameters for the stages ranged from about 1.0 to 0.08  $\mu$ m and the cyclone removed particles down to 3- $\mu$ m diam.

Impactor collection surfaces and the after-filters from seven out of the 60 sample sets were analyzed by INAA at the reactor using a combination of 10-min followed by 3-hr irradiations. At least 26 elements, including Al, As, Br, Ca, Ce, Cl, Co, Cr, Fe, K, La, Mg, Mn, Na, Se, Sb, V, Ti, and Zn, could be detected on at least three of the five submicrometer stages. Only because of the high sensitivity of INAA with the large flux of the reactor was it possible to observe so many elements with a total fine particle loading of only 180  $\mu\text{g}$ . Detection on more stages was generally achieved with loadings of 240 to 400  $\mu\text{g}$ .

We are now performing more extensive studies of detailed size distributions in a variety of settings. Field collections with 3 MOIs were done at suburban Washington sites on the University campus, at Andrews Air Force Base, and at Vienna, VA. Samples were collected in the Ft. McHenry motor-vehicle tunnel in Baltimore, among other things to seek a motor-vehicle tracer to replace the Pb and Br, which have been phased out. Collections were made at urban sites in Philadelphia previously used in studies by this group [3]. These sites are

influenced by several types of industrial sources (e.g., Sb roaster, pigment plant, oil refineries) as well as common urban sources such as motor vehicles, oil-fired power plants and municipal refuse incinerators. We know the chemical signatures for most of these sources, but will be interested here in finding out the detailed size distributions.

Samples from these field studies are now being analyzed by INAA as quickly as possible. About 600 MOI samples have been irradiated for the determination of short-lived nuclides.

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## SOURCES OF AIRBORNE PARTICLES IN AND NEAR MARYLAND AND THEIR WET DEPOSITION

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For several years, first with EPA support and presently with support of the Maryland Power Plant Research Project, we have been determining the concentrations of many elements on airborne particles at various sites in and near Maryland. We resolve the detailed composition patterns of the airborne particles into contributions originating from various anthropogenic and natural sources, relying heavily on concentrations of certain "marker" elements for certain sources, e.g., V and Ni for oil-fired power plants, As and Se from coal-fired plants, Zn, Sb, and Cd from refuse incinerators, etc., a technique called "receptor modeling" [1]. Most

of the analyses of these samples have been performed by instrumental neutron activation analysis (INAA) at the NIST reactor.

Recently, we completed a detailed sampling program in cooperation with Prof. T. E. Church and J. Scudlark, who have long operated a station in Lewes, DE as part of the DOE and, later, EPA network (MAP3S) of about 10 wet deposition stations. Our group collected particulate and gas samples in a filter pack in which the first filter collected particles, followed by three filters impregnated with KOH and glycerol to collect acidic gases. This work was done in two phases. In the first phase, samples

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were collected every 12 hr without regard to rain events. However, the sampler was located close to the Lewes precipitation collector so that results from the two kinds of samples can be correlated later to obtain information about wet deposition efficiencies. In the second phase, an attempt was made to collect air-filter samples for several hours prior to passage of large frontal systems associated with precipitation. When precipitation started, the first sampler was shut off and a second one started. If the precipitation lasted long enough to collect sufficient material for analysis, the second sampler was left on until the rain ended, and a third sample was taken for several hours following the event.

The Lewes sampling ended in Feb. 1990 and in Sept. 1990, we began a sampling program similar to Phase 2 on the grounds of the USDA Beltsville Agricultural Research Center, where there is a station that is part of EPA's Dry Deposition Network.

The base-loaded filters from Lewes have been analyzed by ion chromatography (IC) and we recently subjected all particle filters to "shorts" INAA at the NIST reactor. Preliminary results are listed in table 2 along with comparable data taken earlier by students of this group at the Lewes site and at College Park, MD, about

7 km from the Beltsville site. An additional 30 samples from Lewes have been irradiated for shorts INAA, but the data are not in final form yet. We are beginning to analyze the samples by "longs" INAA, e.g., 2-hr irradiations followed by taking of spectra about 5 days and 3 weeks after irradiations, which will yield data for an additional 20 or so elements. When all of the data are available, they will be subjected to detailed receptor-modeling interpretation. Also, we will compare the airborne concentrations before and after precipitation events with concentrations in rain determined by the Univ. of Delaware group to obtain information on the washout efficiency of the precipitation events. At this time, not many conclusions can be drawn from the limited data set. At Beltsville, we seem to observe the continuation of trends observed earlier by our group, e.g., decreasing concentrations of V, Br and Mn. Vanadium concentrations have been dropping since the 1970s as oil-fired power plants have had to use low-sulfur fuel, which is also much lower in V than the residual oil they used earlier. The major source of Br has been the combustion of leaded gasoline, but as that has been phased out, Br levels have dropped sharply. Likewise, we think Mn levels have gone down over the years

**Table 2.** Preliminary concentrations (ng/m<sup>3</sup>) from Lewes and Beltsville samples\*

Ele- ment	Beltsville Conc	Sept.90-Dec.90 Std. Dev. N	College Park Conc	Nov. 85-Feb.86 Std. Dev N	Lewes Conc	Aug.89-Feb.90 Std. Dev N	Lewes Conc	Feb./Mar. 85 Std. Dev N
Na	835 ± 260	24	604 ± 50	24	1870 ± 200	101	750 ± 90	14
Mg	790 ± 230	18	250 ± 60	23	770 ± 130	84	190 ± 60	13
Al	240 ± 45	24	420 ± 30	24	260 ± 20	102	430 ± 50	14
S	4300 ± 1000	16	2070 ± 600	24	15100 ± 4000	49	1440 ± 150	14
Cl	1080 ± 425	23	770 ± 30	24	1920 ± 300	100	860 ± 115	14
K	360 ± 65	20	167 ± 15	24	340 ± 25	80	200 ± 25	
Ca	440 ± 65	22	480 ± 40	24	465 ± 55	83	303 ± 34	14
Ti	86 ± 19	17	38 ± 10	24	61 ± 10	72	39 ± 9	14
V	3.9 ± 1.0	21	9.1 ± 0.6	24	12 ± 1.0	102	6.4 ± 0.8	14
Mn	5.1 ± 1.1	24	14 ± 2	24	5.4 ± 0.4	97	8 ± 0.9	14
Cu	24 ± 7	15			17 ± 3	58		14
Br	4.1 ± 0.6	22	28 ± 3	24	8.9 ± 0.6	100	17 ± 2	14
In	0.013 ± 0.005	6	0.007 ± 0.009	19			0.012 ± 0.004	
I	1.05 ± 0.19	17	4.7 ± 0.8	24			1.5 ± 0.2	

\*Std. Dev. is standard deviation of the mean value  
College Park data from McCarthy [2]  
Early Lewes data from Kitto [3]

because of the near collapse of the U.S. ferromanganese industry. Some of same trends are observed at the Lewes site; however, the higher V concentrations are probably related to the presence of an oil-fired power plant not too far away at Vienna, MD. Concentrations of some elements such as Na and Cl are strongly influenced by winds that bring marine aerosol to the site from the nearby Atlantic Ocean and Delaware Bay. We are surprised by the high sulfate values, but that will have to be checked carefully, as S is quite difficult to measure by INAA. Note that there are quite a number of missing values for S at both sites. Numbers for them would lower the average. Part of the problem of missing values is the fact that the

sampling durations were governed much of the time by the onset of precipitation; thus, many of the sampling durations were much smaller than optimum. Fortunately, we analyzed only half of each filter, so we may later subject the remaining halves to further analysis, e.g., IC analysis for sulfate.

#### References

- [1] G. E. Gordon, Receptor Models, *Environ. Sci. Technol.* **22**, 1132 (1988).
- [2] L. E. McCarthy, M.S. thesis, Department of Chemistry and Biochemistry, University of Maryland, College Park, 1988.
- [3] M. E. Kitto, Ph.D. thesis, Department of Chemistry and Biochemistry, University of Maryland, College Park, 1987..

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## ELEMENTAL CONCENTRATIONS IN AIRBORNE PARTICLES DEPOSITING IN THE CHESAPEAKE BAY

J. M. Ondov and Z. Y. Wu (University of Maryland, College Park, MD)

Atmospheric deposition is an important source of toxic species including metals such as Cr, Cu, Pb and Zn to some water bodies in the United States, including the Chesapeake Bay, which lies downwind of heavily polluted urban areas running from Norfolk, VA, to Washington, DC, Baltimore, Philadelphia, PA, and Camden, NJ. Prevailing winds from southwesterly to northwesterly directions transport their pollutants, as well as those from the heavily industrialized Ohio River Valley, into the Chesapeake Bay airshed. In addition, eight major coal-fired power stations, i.e., Crane, Brandon Shores, Wagner, Morgantown, Potomac River, Chalk Point, Dickerson, and Possum Point, may adversely influence the Bay airshed.

To better estimate the atmospheric component of these substance to their Bay inventories, the Maryland Department of Natural Resources and the U.S. EPA Chesapeake Bay Liaison Office have initiated a three-year field program involving aerial concentration and precipitation measurements at three sites along

the Chesapeake Bay, e.g., the Wye Research and Education Center at a northern Bay location, a Bay site near the Chesapeake Bay Biological Laboratory at Solomon's Island, and a beach site near the Virginia Institute for Marine Science (VIMS). The work is being conducted by our group in collaboration with the University's Center for Environmental and Estuarine Studies, the University of Delaware, the Virginia Institute for Marine Studies, and Old Dominion University. Aerosol data, consisting of concentrations of selected minor and trace elements in particles of diameter  $< 10 \mu\text{m}$  are being collected by our group for use in estimating dry deposition fluxes to the Bay Airshed.

Particulate samples have been collected continuously for one year at the Wye site, with the assistance of Wye technicians, on 47-mm Teflon fiber filters. Samples are stored under refrigeration at Wye before delivery to UMCP. The first batch of 180 samples is now being analyzed by INAA.

## E. NEUTRON INTERACTIONS AND DOSIMETRY

J. A. Grundl (Ionizing Radiation Division)

The Neutron Interactions and Dosimetry Group develops and applies well-characterized neutron fields and related capabilities for neutron dosimetry methods evaluation and standardization, for detector development and calibration, and for nuclear cross section measurements. Related efforts in cold neutron physics and

metrology provide a basic research component. Involvement with outside organizations, both in the federal and private sectors includes many types of research and technology assistance projects as well as leadership roles on national and international standards and radiation policy making bodies.

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## DOSIMETRY FOR MATERIAL PERFORMANCE ASSESSMENT

Dosimetry methods for monitoring the degradation of materials in high fluence neutron exposures are diverse. This project provides some form of measurement assurance, standardization, or methods development for nearly every approach to materials dosimetry employed in the United States. Interlaboratory measurement cooperation with substantial international participation are an important feature of this project.

LiF Gamma Dosimeters for Davis-Besse Reactor Cavity Dosimetry (D. Gilliam). Nine LiF gamma dosimeters were irradiated in the Davis-Besse Nuclear Power Reactor or at the Three-Mile Island I Reactor and returned to NIST for read out. The welded aluminum dosimetry packages were cut open in Reactor Warm Shop. All the LiF "chips" were found to be in good optical condition and free of radioactive contamination. The optical absorbance of each of the samples was measured twice at three different wavelengths. The samples will be annealed and re-calibrated by  $^{60}\text{Co}$  exposure before results are reported.

NIST/Nuclear Regulatory Commission Contract Work (E. D. McGarry). This contract provides calibrations for reactor pressure surveillance dosimetry that is traceable to NIST standard neutron fission-spectrum fields through

fluence standards, which are radioactive artifacts produced by certified fluence irradiations in the standard fields. NIST also provides consultation and dosimetry assistance for NRC metallurgical test irradiation programs.

Distribution of Neutron Fluence Standards to Provide Benchmark Field Referencing of Neutron Dosimetry for Reactor Pressure Vessels and NRC Metallurgy Test Irradiations (E. D. McGarry). Radiometric dosimeters (e.g. activation foils) are benchmarked for customers by certified fluence irradiation in standard neutron fields, such as the  $^{252}\text{Cf}$  spontaneous fission field or the  $^{235}\text{U}$  fission field at the NIST reactor. The customer measures the specific activity and uses spectrum-averaged cross sections to evaluate his prediction of the NIST certified fluence. Seventeen such fluence standards have been produced this fiscal year.

Fluence standards are routinely produced in the form of 1.25-cm diam radioactive disks. A problem in accurate prediction can arise when the customer's gamma assay equipment has been calibrated for neutron sensors of a different size. The problem can be resolved by simultaneously irradiating both sensors to the same fluence and deriving suitable adjustment factors.

## NEUTRON INTERACTIONS AND DOSIMETRY

Davis-Besse Ex-Vessel Cavity Dosimetry Benchmark Experiment (E. D. McGarry) The power-reactor industry's benchmark irradiation at the Davis Besse Reactor is complete and the dosimeters are being analyzed. Fluence standards have been shipped to B&W for the  $^{58}\text{Ni}(n,p)^{58}\text{Co}$ ,  $^{46}\text{Ti}(n,p)^{46}\text{Sc}$ , and  $^{63}\text{Cu}(n,\alpha)^{63}\text{Co}$  reactions. Fluence standards are also being counted by B&W, Lynchburg Research Center, CEN/SCK, Mol, Belgium, and Arkansas Tech University, Russellville, Arkansas.

NIST has supplied, and will analyze, Paired Uranium Detectors (PUDs) for comparison with other types of fissionable dosimeters. The PUDs in Davis Besse were irradiated together with radiometrics, SSTRs, HAFMs, niobium, and LiF Chips.

Dosimetry Methods Development for Reactor Support Structures (E. D. McGarry) A contract for the dosimetry has been let with the Westinghouse Science and Technology Center to monitor possible radiation damage to structural members at the Trojan Nuclear Power Reactor. The Westinghouse dosimeter-evaluation systems must be benchmarked prior to obtaining the Trojan measured results. Fluence standards were prepared in certified fluence irradiation and shipped in October. The benchmarked dosimetry will be used to make necessary adjustments to the calculations at the dosimeter locations and before extrapolation of radiation (damage) exposure to the support structures. It is now necessary to oversee implementation of the second phase of the contract with Westinghouse to derive the fast neutron fluence on TROJAN Reactor support structures. NIST will consult with ORNL to obtain comparisons of their calculated results with the measured dosimetry for TROJAN.

NRC Regulatory Guide Preparation (E. D. McGarry and J. Grundl) NIST's involvement continues in the development of a draft regulatory guide "Status of a New Regulatory Guide on Methods and Assumptions for Determining Pressure Vessel Fluence." The guide contains advice on up-to-date methodology for carrying out transport calculations assuming use of 2-d discrete-ordinates transport codes. The mechanism for validating calculation is

comparison with measurements. There is also emphasis on validating transport calculations against experimental benchmarks and in-situ surveillance dosimetry.

The guide requires validation of the calculational method against benchmarked dosimetry results. NIST is preparing a NUREG for this purpose as part of a calculational benchmark package.

The Behavior of Np-237 in Ex-Vessel Cavity Fields (E. D. McGarry) The Np-237 response appears to have some correlation to the behavior of non-threshold detectors. This probably is the reason so many experimenters blame unidentified quantities of Pu-239 for low C/E ratios. It is worthwhile to examine several other observations about Np-237 response.

Calculated Response: Although a major issue is the problem in calculating absolute Np-237 accurately, it is also observed that calculated values also show the trend of Np-237 having a non-zero cross section down to very low energies.

Cross Sections: We continue to monitor results from NIST benchmark experiments that consist of Np-237 and other fission isotope responding to various diameter water-moderated spheres around a Cf-252 point neutron source. The results to date gives C/E ratios near unity indicating there is no problem with the Np-237 cross section in the energy ranges of these spectra.

Dosimetry Support for New NRC/HSST Irradiations at University of Michigan (E. D. McGarry) NIST has assumed a dosimetry consultants role for the combined MEA and ORNL operations for the Heavy Section Steel Technology (HSST) Program at the University of Michigan Reactor. The current interest is a result of two circumstances.

There has been a serious decrease in the number of available test reactors with sufficient fluence rate ( $5 \times 10^{11}$  n/sec) to efficiently do HSST steel experiments, and the 2 MW University of Michigan Reactor has space in their pool for several rather large experiments. Specifically, tailored spectrum experiments will be undertaken, in which the epithermal fluence is enhanced by several orders of magnitude over the fluence greater than 1 MeV.

## RADIATION PROTECTION DOSIMETRY

Standard neutron fields are used to calibrate radiation protection instrumentation and to investigate and test new types of dose measuring techniques. Responsibilities in national and international dosimetry methods research focuses on tissue dose modeling, and tissue equivalent proportional counter (TEPC) measurements, and the development of written standards.

Calibration Services (E. Boswell and R. Schwartz). Approximately 35 neutron instruments were calibrated this year. Although the majority were conventional radiation protection instruments, calibrations were also done for neutron flux monitors used at radiation therapy installations, and fission chambers for use at reactor sites.

ICRU Publication on Practical Determination of Dose Equivalent (R. Schwartz). As far as can be determined we are through with our ICRU report, entitled "Measurements of Dose Equivalent from External Photon and Electron Radiations". The report was approved by the main commission last winter, revised a few times since then, and should be ready to go.

ISO Document on Instrument Calibration (R. Schwartz). The final draft of the standard "Procedures for Calibrating and Determining the

Response of Neutron Measuring Devices Used for Radiation Protection" is being sent off to the member countries for comment before final publication as an ISO standard. We are already preparing a revised version of the standard to take into account some new work which has recently been published.

Measurement of Neutron and Gamma-Ray Kerma Rates at AFRRI (C. Eisenhauer, J. Grundl, R. Schwartz). Two sets of on-site measurements were performed at AFRRI to resolve a discrepancy between ratios of neutron and gamma-ray kerma rates determined with tissue-equivalent ionization chambers (TEIC) and tissue equivalent proportional counters (TEPC). The ratio obtained in one particular field with TEIC only led to anomalous results for the relative susceptibility of mice to neutron and gamma radiation. Neutron reaction rates obtained with NIST fission chambers corroborated both concurrent and earlier measurements of neutron kerma rates with TEPC. It was concluded that TEIC do not respond properly in fields with a high neutron to gamma ratio. Using the consistent ratio from TEPC and fission chambers, the neutron quality factor for mice no longer appeared anomalous.

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## RESEARCH AND TECHNOLOGY ASSISTANCE

Research and technology assistance are strongly coupled in neutron dosimetry. A multiplicity of institutional involvements, drawn to the group by the availability of unique irradiation facilities and measurement capabilities, encourages a variety of attractive projects and unavoidable responsibilities.

Benchmark Measurements for Criticality Safety (D. Gilliam). The transport of  $^{252}\text{Cf}$  neutrons through spherical water moderators has been studied by observing fission rates of four isotopes in the leakage spectrum outside the moderator. Both measurements and Monte Carlo calculations with highly detailed modelling of the experiments have been compared and

reported for two different water radii [1]. The calculations tended to over-predict the thermal flux, especially for the thicker moderator.

### Reference

- [1] D. M. Gilliam and J. F. Briesmeister, "Benchmark Measurements and Calculations of Neutron Leakage from Water Moderators," Proceedings, International Topical Meeting on Advances in Mathematics, Computations, and Reactor Physics, Pittsburgh, April, 1991.

Neutron Fluence Rate Measurements at the CNRF (D. Gilliam). The fluence rate was measured at four wavelengths for the beam coming from the velocity selector and going to

the 30 m SANS instrument on the NG7 beam. The  $^{239}\text{Pu}$  fission rate was found to drop by about a factor of 2 for each increase of wavelength of 2 angstroms.

At the NG6 end-station, fluence rates for both fast neutrons and cold neutrons were measured for several different filter configurations.

Calculations of Slab Penetration (C. Eisenhauer). Results of a basic study of slab transmission and reflection by neutrons and gamma rays were published in *Nuclear Science and Engineering*. Abstract is as follows:

Using Monte Carlo calculations, it is shown that the transmission of scattered neutrons or gamma rays from a point source through a plane slab of infinite extent to a point detector depends on the orientation of the slab but varies very little with the slab position. This is also true for reflected radiation if the source is replaced by its image source and the results are interpreted in terms of a transmission problem. It is also shown that the transition from a slab of small extent (narrow beam conditions) to a slab of infinite extent (broad beam conditions) can be characterized by a simple function of the single-scatter angle. This function, too, can be applied to reflected radiation by invoking the image source. Typical results are presented for polyethylene and iron.

Upgrading Neutron Transport Computational Capability and Converting All Radiation Transport and Related Codes to the Cray Computer (C. Eisenhauer). The 2-d discrete ordinates code, DORT, has been acquired and some sample problems have been run on the Cray. All neutron and photon transport codes, including ANISN and MCNP, are being converted from the NIST CYBER 205 computer to the new NIST Cray Y-MP Computer. The DETAN code for dosimetry analysis and miscellaneous smaller codes are already on the Cray. The MCNP and YSPEC codes will be operational by the end of FY 91.

Calculations of Transmission of Neutrons Through Iron Shells (C. Eisenhauer). There is a long-standing question regarding the accuracy of the inelastic cross section in iron used to calculate fast neutron gradients in thick steel. This is a critical issue for predicting the useful service life of power reactor pressure vessels.

In preparation for a benchmark program of iron shell transmission measurements at NIST, a series of calculations of the transmission of neutrons from a point fission neutron source through spherical shells of iron have been performed. The endpoint of these benchmark measurements will be to assess the adequacy of recently revised inelastic cross sections for iron.

Two-Component Room-Return Model (C. Eisenhauer). Accurate calibration of neutron personnel instruments requires a correction for the effect of neutrons reflected from the walls of the calibration room. The current model for making this correction, derived from reflection in a spherical cavity, predicts a constant fluence of room-return neutrons over the volume of the room. Actual calibration rooms are usually rectangular parallelepipeds for which the room return fluence will vary with position. A modified room-return model has been devised which treats the first reflection as if it were from a plane slab, and the second and higher orders of reflection according to the original spherically symmetric model. The model for first reflection establishes a variation with position. The two-component model agrees well with Monte Carlo calculations and with experiment.

NIST/Westinghouse Cooperative Agreement for Measurement Assurance (E. D. McGarry). Measurement assurance activities for Westinghouse radiometric (activation foil) and Solid State Track Recorder (SSTR) dosimetry continues. NIST is especially interested in problems with reliable masses for SSTR fissionable deposits that are in the nano-gram to pico-gram range, and which were developed by Westinghouse Industrial Technology Center. The SSTR dosimeters provide for the registration of fission products tracks in mica disks place next to thin deposits of select fissionable material. The track density for uniformly thin fissionable deposits is proportional to fast neutron fluence. The absolute accuracy of the technique has been validated at NIST through controlled irradiation experiments in standard neutron fields.

SSTR Ultralight Mass Determination (E. D. McGarry). Mass determinations require NIST provide known fluences to the ultra-lightweight SSTRs and Westinghouse measure their response and deduce masses. The irradiations are carried

out in the  $^{235}\text{U}$  Cavity Fission Source at the NIST Reactor, to an accuracy of about 2.5% ( $1\sigma$ ).

High  $T_c$  Research (S. F. Trevino, F. J. Owens, and E. D. McGarry). The structure of a variety of high critical temperature ( $\text{Hi-}T_c$ ) superconducting materials are being developed and studied at NIST. One material containing [B-Pb-Sr-CuO] may have properties that are dependent upon the state of the CuO. The current density that this materials can sustain is

a function of the mobility of the microscopic magnetic flux vortices. Speculation that atomic defects may effectively trap the vortices is being tested.

Use has been made of the NIST  $^{235}\text{U}$  neutron fission spectrum irradiation facility to introduce controlled amounts of displaced atoms (i.e., defects) in the material by performing certified fluence irradiations, which are free of lower-energy neutrons that cause complicating neutron capture transmutations.

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## IRRADIATION AND CALIBRATION FACILITIES

Well-characterized neutron fields built and maintained as permanent irradiation facilities, provide certified fluences of pure fission neutrons, sub-MeV distributions, monoenergetic keV beams, and thermal neutrons. Passive and active detectors are exposed in these neutron fields for response calibrations, for cross section measurements, and for the investigation of new measurement techniques. A multipurpose fission rate measurement capability is centered around the NIST "go anywhere" double fission chambers and the NIST set of fissionable isotope mass standards (FIMS). The Manganous Sulfate Bath is the primary neutron source strength calibration facility for the United States. Absolute neutron fluences for all fission-neutron-driven standard neutron fields at NIST are derived from source strength calibrations at this facility.

Design and Construction of the Materials Dosimetry Reference Facility (MDRF) (J. Grundl, C. Eisenhauer, and E. D. McGarry). A new, high-intensity reference neutron field for reactor dosimetry, designed and constructed by NIST, will be operated at the University of Michigan 2MW Research Reactor. Certified fast-neutron fluence irradiations and related validation experiments, traceable to NIST, are to be performed in support of neutron dosimetry for the nuclear power and metallurgical-test communities.

The development of this benchmark facility is a natural extension of the long-term NIST

program to develop standard neutron fields for measurement assurance applications in materials dosimetry, and the testing of new dosimetry detectors and techniques. The primary user of this irradiation facility will be industry and government organizations that have major responsibilities to assess the integrity of high-risk nuclear power reactor components and more generally to establish the data base that describes radiation damage in steel.

The MDRF complements existing fission neutron standard fields at NIST by providing a tenfold increase in fast-neutron fluence, a much larger irradiation volume with modest flux gradients, and a neutron spectrum rich in intermediate-energy neutrons. For the latter, the MDRF offers two spectrum options by operating with or without a boron-10 filter. A number of detector response characteristics and methods of dosimetry interpretation can be investigated with this choice.

Essentially, the MDRF is a 15.2 cm diam steel cylinder with an axial bore mounted in the pool near the face of the Michigan research reactor. Irradiation thimbles, inserted from the top of the pool, will locate samples mounted inside at the core midplane and can also accommodate active instruments such as NIST double fission chambers. Two separate thimbles, one with and one without a boron-10 liner, allows a convenient change from a neutron spectrum that goes down to the cadmium cut-off at 0.4 eV to one which cuts off at about 5 keV.

## NEUTRON INTERACTIONS AND DOSIMETRY

Estimated neutron fluence rates with the MDRF close to the reactor are as follows:

without  
boron-10:     $4\text{E } 11 \text{ cm}^{-2}\text{s}^{-1}$      $>1 \text{ MeV}; 1.7\text{E } 12 >0.4 \text{ ev}$

with  
boron-10:     $4\text{E } 11 \text{ "}$      $>1 \text{ MeV}; 1.1\text{E } 12 >5 \text{ Kev}$

Certification of the neutron fluence for dosimetry calibration and performance validation irradiations will be established on the basis of neutron fluence transfer from the NIST Fission Neutron Irradiation Facilities. It is anticipated that the neutron fluence above 1 MeV will be specified to an uncertainty better than 10%. Specification of the total neutron fluence will be more uncertain because of a much greater dependence on calculation.

A three-group summary of the neutron energy distributions in MDRF, based on scoping calculations, is as follows:

	0.4ev	0.1 MeV	1 MeV	18 MeV
w/o B10:	0.45	0.33	0.22	
w/B10:	0.18	0.48	0.34	

Main features of the neutron spectra are the mild departure from a fission spectrum in the MeV energy range, the relaxation into a 1/E spectrum below 1 keV for the MDRF without the boron-10 filter and the cut-off in the keV range with the filter.

A thorough characterization of the neutron spectrum will come from a combined interpretation of 2-d neutron transport calculations and benchmarked reaction rate measurements with threshold and low-energy detectors. A special feature of the spectrum tailored with a boron-10 filter will be the determination of the boron-10 thickness by means of a neutron transmission measurement in the 2 keV filtered beam at NIST. The effective nuclear thickness obtained in this way removes all or most of the uncertainty in boron-10 enrichment, powder density in the thimble, and the absolute cross section scale for neutron absorption.

Activation detector calibrations planned for the MDRF will serve on-going and planned steel irradiations by Materials Engineering Associates

and by ORNL at the U. Michigan Reactor, pressure vessel dosimetry contracts at the Westinghouse Nuclear Technology Division, and surveillance capsule backfitting and cavity dosimetry projects at B&W. Expected dosimetry measurement assurance requirements proposed by the Nuclear Regulatory Commission may be conveniently and inexpensively served by the MDRF.

Continued development and calibration of Solid State Track Recorders (SSTRs), a dosimetry detector of great promise for reactor pressure vessel damage monitoring, will be substantially enhanced by the availability of the MDRF. A new generation of fission dosimeters in the form of paired uranium detectors (PUDS), sintered wires, and encapsulated beads can also be investigated and validated in the two component neutron fields of the MDRF.

Examples of attractive research opportunities are: (1) the iron inelastic scattering cross section discrepancy, crucial for the pressure vessel embrittlement uproar; (2) establishing Nb(n,n') activation as a practical main-line reactor dosimetry detector; and (3) determining proper corrections for subthreshold fission in Np, U234, and U236.

Calculations for the MDRF (C. Eisenhauer). The design of the MDRF required scoping calculations to explore the sensitivity of fluence intensity and spectrum to variations in design parameters. Accordingly, four types of 1-d neutron transport calculations were performed with the ANISN discrete ordinates code to simulate the actual cylindrical configuration. The first was a study of the spectrum at the center of an iron slab in water near the core of the reactor as a function of iron thickness. The second was a comparison of spectra in slab and cylinder configurations. The third calculation used the output spectrum from the slab calculation as input to the exterior cylindrical surface of the detector configuration. Finally, we studied the effect of a cylindrical sleeve of  $^{10}\text{B}$  on the fluence spectrum at the center of the cylindrical array. Results were adequate to decide upon a final configuration and proceed with the final design.

## COLD NEUTRON PHYSICS AND METROLOGY

Research activities in low energy neutron physics involves experiments in neutron beta decay and weak interaction physics, and the development of advanced techniques in neutron

optics and interferometry. Strong collaborations, both foreign and domestic, exist with national laboratories, universities and independent research laboratories.

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### NEUTRON BETA DECAY

M. S. Dewey, D. M. Gilliam, G. L. Greene, and W. M. Snow  
(Ionizing Radiation Division)

and

G. P. Lamaze (Nuclear Methods Group)

The free neutron is a beta unstable particle which decays with a mean lifetime of  $\sim 900$  sec. Because neutron decay is the simplest nuclear beta decay, measurements of the parameters which characterize neutron decay can be directly related to the fundamental theory describing weak nuclear interactions. An accurate knowledge of the neutron lifetime is also important in a variety of astrophysical contexts which range from the production rate of neutrinos in the sun to the details of nucleosynthesis during the Big Bang. In addition, detailed measurements of correlations between the particles (protons and electrons) created in neutron decay can provide a precise test of fundamental symmetry principles. The NIST program in neutron beta decay has several aspects and is a collaborative effort between several institutions. A current major effort involves the accurate determination of the neutron lifetime. This project evolved from a collaboration between NIST, the University of Sussex (U.K.), the Central Bureau for Nuclear Measurements (E.E.C., Geel, Belgium) and the Scottish Universities Research and Reactor Center (Glasgow). The current program centered at the NIST Cold Neutron Research Facility follows on work carried out at the Institut Laue Langevin in Grenoble. A second experiment will use the lifetime apparatus to determine energy spectrum of the decay protons created from neutron decay. A third project involves a determination of the correlation between the momenta of the decay electrons and

protons from the decay of polarized neutrons. The observation of a nonzero triple correlation between the spin vector of the decaying neutron and the momenta of the decay proton and electron would imply a violation of time reversal symmetry (T). This T violation experiment is a collaboration between NIST, Los Alamos National Laboratory, and Harvard University.

The neutron decay detector to be employed for the neutron lifetime experiment has been extensively rebuilt in the last year with the completion of an all new precision electrode assembly, new mechanical supports, new data collection electronics and new high voltage electronics. The improved apparatus is currently ready to accept beam at neutron guide six (NG-6). With minor additions to the control electronics this apparatus will be employed for the determination of the decay proton spectrum.

The apparatus to be used for the T violation experimental will consist of two major components. One component is a neutron decay detector capable of detecting both the electrons and proton emitted in neutron decay. This detector has been developed as a Los Alamos, NIST, Harvard collaboration and will be installed for preliminary testing in late 1991. The other component in the T violation apparatus is a novel neutron polarizer based on optically pumped  $^3\text{He}$ . This polarizer is under development at Harvard University. A prototype will be tested at CNRF in late 1991/early 1992.

ABSOLUTE DETERMINATION OF NEUTRON FLUX

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T. Chupp and J. Richardson (Harvard University, Cambridge, MA)

H. Robertson and J. Wilkerson (Los Alamos National Laboratory, Los Alamos, NM)

J. Pauwels (Central Bureau for Nuclear Measurements, Geel, Belgium)

and

R. Scott (Scottish Universities Research and Reactor Center, Glasgow, UK)

The present state of the art in the absolute determination of thermal and cold neutron fluxes allows measurements with an accuracy of  $\sim 1/2$  of one percent. In addition to the obvious gains in the accuracy of neutron detectors and dosimeters for low energy neutrons, there are a variety of other motivations for a program which would improve this level of precision.

In particle physics, recent measurements of the beta decay lifetime of the neutron have required, as a calibration, a determination of a neutron capture flux to scale an observed neutron decay rate. The uncertainty in this calibration contributed approximately one half of the total error in the neutron lifetime determination. In chemistry, the accuracy of the analytical method of prompt neutron activation analysis is ultimately limited by the knowledge of the neutron flux at the activation position. In nuclear physics, the accuracy of several important neutron capture cross sections may be improved if better techniques for neutron flux determination were available. In nuclear metrology the activity of standard neutron sources could also be determined with improved precision.

Our program for improving the technology for absolute neutron flux determination involves several related measurements and the collaboration of a number of institutions. Among these institutions are Los Alamos National Laboratory, The Central Bureau for Nuclear Measurements of the EEC, Harvard University, and the Scottish Universities Research and Reactor Center (Glasgow). Two specialized neutron detectors have been constructed and are presently undergoing initial testing. Both of these detectors have the characteristic that they completely absorb (nearly) all neutrons which enter the detector. For this reason these new instruments are known as "black" detectors.

The first of these new black detectors is calibrated by detecting, in coincidence, both the alpha particles and gamma rays produced in the capture of thermal neutrons on  $^{10}\text{B}$ . Such a coincidence measurement allows the determination of the absolute efficiency of both the alpha and gamma detectors. By alternately employing "thin" and "thick"  $^{10}\text{B}$  targets, it is possible to configure the detector so that it stops essentially all neutrons and detects emitted gamma rays with well known efficiency. This detector was installed on neutron guide 6 (NG-6) in July of 1991.

The second "black" detector is based on a quite different, calorimetric calibration scheme. In the calorimeter, a neutron beam is totally absorbed in a  $^6\text{Li}$  rich target. Neutron capture on  $^6\text{Li}$  leads to the production of alpha particles and tritons with a well known total energy release. These particles have a very short range in the target and essentially all of their kinetic energy is deposited as heat in the target. At cryogenic temperatures, ( $\sim 5\text{ K}$  in the present apparatus) the heat capacity of the target is sufficiently small that this heat is easily detected. This neutron calorimeter can be calibrated by comparing the nuclear heating with Joule heating from well characterized current and voltage sources. The neutron calorimeter project is a collaborative effort between NIST, Harvard University, and Los Alamos National Laboratory. It is anticipated that this detector will have its initial tests in late 1991.

The most accurate traditional method for the determination of neutron fluxes employs well characterized depositions of  $^{10}\text{B}$  and  $^6\text{Li}$ . These materials are selected for the large and well known  $(n,\alpha)$  cross sections. If such a target is placed in a neutron beam and is "viewed" with an alpha particle detector of known solid angle, the incident neutron flux can be deduced from the alpha count rate and the product of the areal

density of the deposit, the cross section and the detector solid angle. At present the limitation to the accuracy of this method lies in the ability to accurately determine the areal density of the deposits. Thus, another aspect of this flux determination program involves better preparation and characterization of such deposits.

This work is being carried out as part of a cooperative program with the Central Bureau for Nuclear Measurements of the European Community. New evaporation systems and other apparatus have been acquired and fabricated at NIST and CBNM (Geel, Belgium).

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### NEUTRON INTERFEROMETRY

M. Arif, M. S. Dewey, and G. L. Greene  
S. Werner and H. Kaiser (University of Missouri, Columbia, MO)  
A. Zeilinger (University of Innsbruck, Austria)  
and  
A. Klein and G. Opat (University of Melbourne, Australia)

The quantum mechanical description of particle dynamics implies that the neutron has a wavelike as well as a particle like character. This wavelike character in turn implies that neutrons can exhibit interference phenomena analogous to that familiarly encountered in optical interferometry. The neutron interferometer facility under construction at the guide hall of NIST's Cold Neutron Research Facility will be employed to investigate a variety of phenomena using interferometric techniques. While much of the phenomenology of neutron interferometry is similar to optical interferometry, there are several essential differences which make neutron investigations more challenging technically, as well as potentially more interesting scientifically. Cold and thermal neutrons have wavelengths which are typically three orders of magnitude less than the wavelength of light typically used in optical experiments. This and other factors imply that neutron interferometers are significantly more sensitive to environmental perturbations than optical systems. While this poses serious experimental challenges, it also promises novel scientific opportunities.

The optical elements to be employed in the NIST neutron interferometer will be fabricated from "perfect" crystal silicon crystals. The use of perfect crystal optical components implies that the wavelengths of the neutrons to be used will be on the order of the atomic spacing in the

crystal lattice. As this is typically three orders of magnitude less than the wavelength of visible light, such a neutron interferometer will be far more sensitive to vibration than optical devices. Much of the work over the last year was devoted to the design and construction of an environmental isolation system to reduce seismic and acoustic interferences.

A schematic of the vibration isolation under construction is shown in figure 1. To attain the requisite degree of vibration reduction the system employs two stages of isolation. The first stage is a large reinforced concrete slab supported by airsprings with a characteristic frequency of approximately 2 hertz. The second stage is a granite table also on airsprings with a somewhat lower resonant frequency. In combination, these two stages of isolation provide a noise rejection which is multiplicative. Both of these airspring systems employ a long term positional servo system which was developed at NIST and is now a commercial product. The secondary airspring system will also be equipped with a high band width magnetic actuator which may ultimately be used to "lock" the upper table to an inertial test mass. Much of our efforts this year have been devoted to development and construction of this system. The neutron interferometer facility will employ monochromatic neutrons. These neutrons will be extracted from NG-7 using a novel in-guide monochromator. This monochromator (fig. 2) provides control of two

## NEUTRON INTERACTIONS AND DOSIMETRY

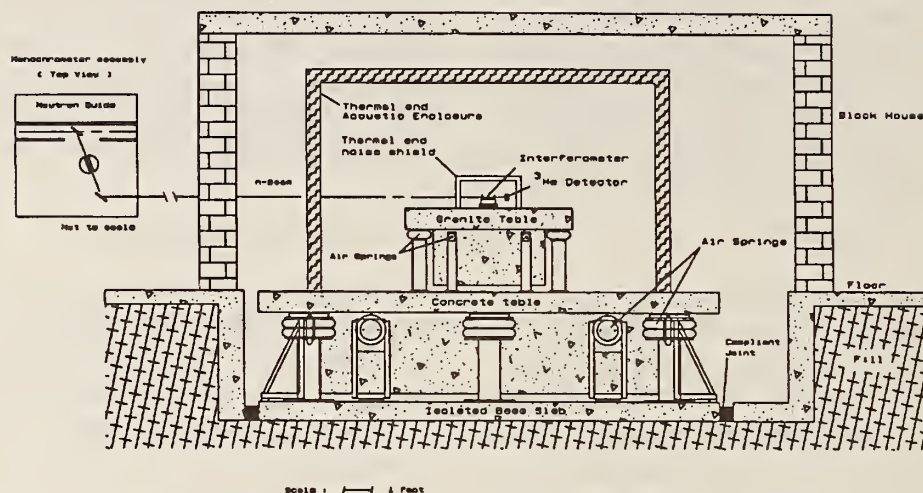


Figure 1. Schematic of the NIST neutron interferometer setup.

axes of motion of the monochromating crystal using a quadrilateral flexure. The neutrons reflected off the monochromating crystal (pyrolytic graphite in the first instance) exit the guide through a single crystal silicon "window" coated with a thin layer of  $^{58}\text{Ni}$ . This window transmits, with high efficiency, the reflected neutrons. However, the unreflected beam continues with the window acting as a normal neutron guide surface. This procedure allows the insertion of a monochromator without the need for a break in the guide. This will reduce background as well as reducing beam attenuation from windows and guide gap losses. The design and operation of the neutron interferometry facility is a collaborative effort between NIST and the University of Missouri (Columbia). This work is supported by NIST and the National Science Foundation. Additional scientific collaboration involves faculty and students from the University of Vienna and the University of Innsbruck (Austria) as well as the University of Melbourne (Australia).

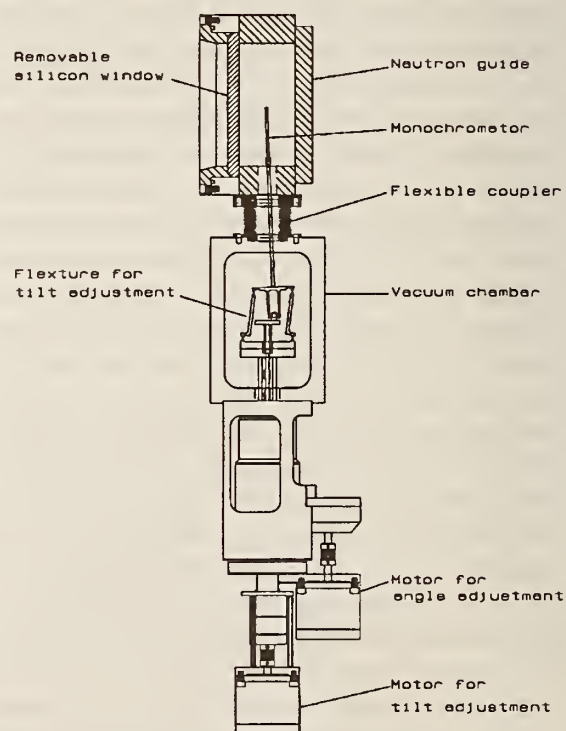


Figure 2. Diagram of the monochromator assembly which would allow rotation as well as tilting of a monochromator inside the guide.

# THE ELASTIC DEFORMATION OF A MONOLITHIC PERFECT CRYSTAL INTERFEROMETER: IMPLICATIONS FOR GRAVITATIONAL PHASE SHIFT EXPERIMENTS

H. P. Layer  
and

G. L. Greene (Ionizing Radiation Division)

Colella, Overhauser and Werner [1] (COW) first observed the quantum mechanical phase shift induced by a gravitational potential on a massive particle (neutron). Their experiment employed monolithic, perfect crystal neutron interferometer whose orientation was varied with respect to the local gravitational field (fig. 1). This and subsequent [2,1] experiments remain unique in that a distinctly quantum mechanical observable is influenced by gravity. The COW experiment may be viewed [2] as an equivalence principle test taken to a strong quantum limit, or alternatively, as an essentially quantum method for the determination of  $g_n$ , the local acceleration of gravity for free neutrons.

The principle of the COW experiment is exhibited in figure 1. An input beam of thermal neutrons is incident on the first plate of an Laue-Laue-Laue monolithic interferometer. This interferometer is fabricated from a "perfect" single crystal of silicon having no dislocations within its volume. In analogy with optics, an intensity modulation at counter C2 or C3 will appear if a phase shift is introduced between paths ACD and ABD. In the COW type experiment, this phase shift is introduced by rotating the interferometer about line AB.

This gravitational shift must be corrected for several additional effects [3] the Sagnac phase shift, which results from the Coriolis acceleration due to the rotation of the earth, 2) corrections [3,4] which result from the Borrmann effect, and 3) dynamical diffraction corrections which arise because the diffraction is taking place in a non-inertial frame. Finally, there is the instrumentally induced phase shift which results from the elastic deformation of the interferometer which depends on the rotation angle of the interferometer. In the experiment of Werner, Kaiser, Arif, and Clothier, the phase shift due to elastic deformation was measured by repeating the COW experiment with x-rays.

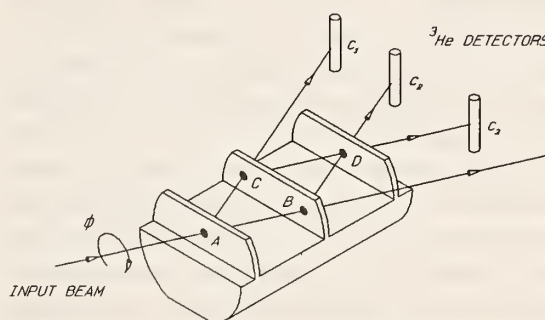


Figure 1. Experimental geometry to measure neutron phase shift.

From such measurements it was observed that the phase shift due to elastic deformation,  $\Delta\beta_{\text{bend}}$ , was proportional to  $\sin\phi$ .

In view of the basic nature of the theory which is tested in the COW experiment (non-relativistic quantum mechanics and Newtonian gravity), it is disconcerting to note that the two most accurate COW experiments [2,3] yield results which disagree with theory by several times the quoted error. The final results of Werner, Kaiser, Arif, and Clothier can be summarized by an experimental and theoretical value for  $\Delta\beta_{\text{grav}}$ . These were (in radians):

$$\begin{aligned} \text{experiment: } \Delta\beta_{\text{grav}} &= (58.72 \pm 0.03)\sin\phi, \\ \text{theory: } \Delta\beta_{\text{grav}} &= (59.19)\sin\phi. \end{aligned}$$

The discrepancy of  $\Delta\beta_{\text{theor-exp}} = (0.47 \pm 0.03)\sin\phi$  is well outside experimental error.

The method used to experimentally measure  $\Delta\beta_{\text{bend}}$  assumes that the neutron and x-ray beams had the same lateral extent. That is, they "interrogated" the same regions of the silicon monolith, and, thus, were influenced by the gravitationally induced deformation in the same way. It is our hypothesis that this was not the case, and 1) the neutron diffraction occurred over an area of greater lateral extent than the x-rays, and 2) the gravitationally induced

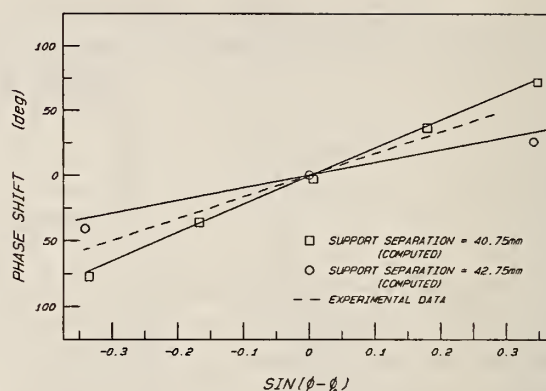
deformation caused the plates to be curved in the lateral direction. The result is that the x-ray diagnostic did not accurately measure  $\Delta\beta_{\text{bend}}$  for neutrons.

In this paper we calculate the elastic deformation of the monolithic interferometer used in the COW experiments using the finite element method. We will analyze the recent measurement of Werner, Kaiser, Arif, and Clothier [3] in which considerable attention was paid to the deformation problem. However, our conclusion will also be applicable to the original COW experiments [1,2].

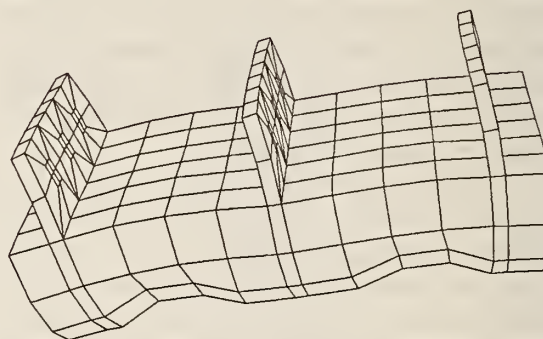
The model used in the finite element calculation is made by subdividing the monolithic interferometer into smaller regions, each of which is in the shape of an irregular 8-node brick. Boundary conditions are established by rotating the model into the appropriate orientation, fixing the positions of the support nodes and imposing a gravitational force at the centroid of each brick. Handbook values for the elastic constants and density of silicon were used and isotropy was assumed. The program calculates the stress and displacement at each node. Considerable effort was taken to duplicate the dimensions of the silicon interferometer and to design the mesh (the placement and size of the nodes and elements) to insure accurate results.

The finite element method analysis has correctly reproduced the angular dependence of the x-ray gravitationally induced phase shift, figure 2, and, in addition, has identified local variations of the deformation which affects the neutrons differently than the x-rays, figure 3. The magnitude of the calculated result agrees well with the measured discrepancy.

By remeasuring the gravitationally induced x-ray path length change over a larger region which more accurately represents the neutron diffraction region, one can expect a further resolution of this problem.



**Figure 2.** Plot of the calculated and observed X-ray gravitationally induced phase shift as a function of interferometer rotation about the axis of the input beam. This comparison was used to establish the accuracy of the finite element analysis.



**Figure 3.** Calculated shape of the deformed interferometer showing tilt and curvature of the plates. The scale of deformation is greatly exaggerated.

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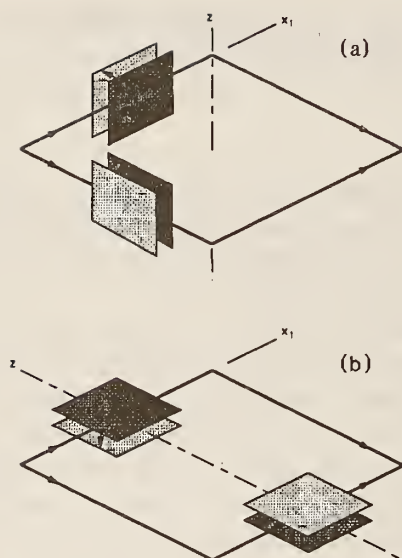
## THEORETICAL ANALYSIS OF FUNDAMENTAL TESTS OF QUANTUM MECHANICS VIA NEUTRON INTERFEROMETRY

R. C. Casella

The discoveries in 1957 that the laws of nature are not invariant under mirror reflection (P) and in 1964 under the combined operation CP (where C denotes exchanging matter with antimatter) led some physicists to suspect the fundamental CPT theorem, which follows from little more than causality, i.e., local coupling between particles and their fields. Because of its deep origins, most physicists bet on CPT, whence yet another heretofore sacrosanct microscopic symmetry, time reversal (T) would have fallen. An analysis by the author in the late sixties of the (rather crude) data then available showed that the latter was indeed true [1]. To this day, CPT (and local coupling) remain valid as they come under ever-closer experimental scrutiny. Paradoxically, quantum mechanics manifests a nonlocal aspect in that the results of certain experiments depend only on the so-called "topological charge" contained between classically distinct orbits traversed by one and the same particle, but are otherwise independent of the detailed orbits. These nonlocal effects and their topological nature, first discussed in the context of neutron interferometry by Aharanov and Casher (AC) [2], have been observed in pioneering experiments by a team led by S. A. Werner at University of Missouri, at Columbia, MO and G. Opat and A. Klein of the University of Melbourne, Australia [3]. The interpretation of these experiments has been the subject of some controversy as has the AC effect, itself. Is the AC effect topological? If not, in what sense is the action of static electric fields on the passage of neutrons through an interferometer nonlocal? Does the neutron experience an acceleration? Is the effect really the dual of the (magnetic) phase

shift induced by an isolated coil on charged particle, i.e., the effect introduced earlier by Aharanov and Bohm (AB)? Is there an experimental way to tell?

In the previous progress report [4] I showed how to apply the path integral technique (introduced by Dirac and developed by Feynman) to arrive at an especially clear way of viewing these experiments. I subsequently was led to suggest a new experiment to demonstrate that while the AC effect *is indeed topological in a two-dimensional context*, the phase shifts introduced by static electric fields are *in general not topological*, but are nonetheless nonlocal in that the measured phase shift results from the transport along classically distinct paths of the quantized spin of a single neutron. Such an experiment, which is illustrated in figure 1, could be carried out at the interferometer currently under construction at the CNRF at NIST. Although the electric-field-induced phase shifts are nonlocal in the sense discussed, the *coupling* is always *local*. In the AB effect the charge couples locally to the magnetic vector potential  $A$ . In the AC effect and in the experimental configuration I have suggested the magnetic moment of the neutron couples locally to the magnetic field  $\mathbf{B}' = -\mathbf{v}/c \times \mathbf{E}$  that exists in the neutron's rest frame. Thus, no conflict with the CPT theorem exists and the latter remains best tested via  $K^0$  (and possibly  $B^0$ ) experiments. Answers to the other questions have also been obtained and the results published in a Physical Review Letter [5]. Subsequently, I have begun to examine the theoretical underpinnings and physical implications of yet another novel neutron-interferometer experiment, which has been proposed by S. A. Werner [6].



**Figure 1.** Arrangement of the capacitor plates in a neutron interferometer (a) as in reference [3] where the axis of spin quantization is normal to the orbital plane and (b) in the proposed experimental setup where the axis lies in the orbital plane. In (a) the electric field  $E$  lies within the orbital plane. In (a) the electric field  $E$  lies within the orbital plane whereas in (b) it does not. For simplicity, the crystal mirrors have been omitted from the diagrams. [Here,  $z$  labels the invariant axis of spin quantization, and  $x_1$  the path variable along the first leg of the trajectory;  $y_1$  (not shown) is such that  $(x_1, y_1, z)$  is a right-handed triad. In (a) the axes are rotated about  $z$  at each mirror such that  $x_1$  denotes the path variable (see text). In (b)  $x_1$  denotes the path variable along the active legs. Along the legs where  $E$  is null the path variable is  $-z$ , but the field-induced phase-change integrals vanish there. The physics, of course, is independent of the arbitrary labels and the quantization axis acquires a sense physically only in the presence of a polarizing biasing field.]

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## F. FACILITIES, OPERATIONS, AND TECHNIQUE DEVELOPMENT

A significant part of on-going research programs includes the design and construction of new instruments. Associated with this is development of neutron experimental and data-analysis techniques to utilize available flux in the most efficient manner possible. In this section,

new instrumentation and methods—primarily related to the CNRF—are described. Also included are a summary of reactor operations and engineering activities for the year, and some developments in the area of health physics relevant to NBSR-based programs.

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### COLD NEUTRON PROJECT

G. M. Baltic, J.R.D. Copley, D. H. Fravel, C. J. Glinka, J. A. Gotaas,  
G. C. Greene, W. A. Kamitakahara, W. C. Knill, J. G. LaRock, H. P. Layer, C. J. Majkrzak,  
C. O'Connor, D. J. Pierce, H. J. Prask, M. J. Rinehart, J. M. Rowe, S. K. Satija, I. G. Schröder,  
T. Thai, T. J. Udovic, and R. H. Williams

In the period from October 1990 through May 1991 four instruments of the CNRF became operational: the 8-m SANS spectrometer, the cold neutron depth-profiling station, the cold neutron prompt-gamma activation analysis spectrometer, and the 30-m NIST/Exxon/U. of MN SANS spectrometer. The neutron lifetime determination apparatus at the fundamental neutron physics station, the CHRNS 30-m SANS spectrometer (part of the NSF/NIST Center for High Resolution Neutron Scattering), and the medium resolution time-of-flight spectrometer are all being installed. All of the completed stations have already been used for NIST, collaborative, and independent guest researcher experiments, the details of which are given elsewhere in this report. Design of the new, hydrogen cold source is nearing completion, and a new higher capacity He refrigerator has been delivered to Reactor Radiation Division (RRD). The CNRF, which is a response to a critical national need for a cold neutron measurement capability, is a National Facility; to this end, the experimental stations installed are available to the scientific and engineering community on the basis of scientific merit of proposals or in Participating Research Teams. The Program Advisory Committee (PAC) has a critical role in advising NIST on the utilization of the facility. In February 1991 the PAC for the CNRF met at NIST for the second time along with the newly constituted Executive Committee (EC) of the CNRF Researchers' Group. The PAC members

are S. K. Sinha, Exxon Research and Development Corp.; D. L. Price, Argonne National Laboratory; E. A. Schweikert, Texas A&M University; and H. Yu, University of Wisconsin. EC members are Chairman T. P. Russell, IBM, San Jose; R. Cappelletti, Ohio University; T. Hossain, Texas Instruments; and J. Weertman, Northwestern University. In this meeting, organized primarily by Bill Kamitakahara—the NIST scientific coordinator for the program, final recommendations and timelines were proposed for the CNRF researcher program. Based on the recommendations made, details of the program have been developed with the following actions taken:

- The first Call for Proposals was sent out to researchers at U.S. university, industrial, and government laboratories in mid-June.
- The deadline for proposal submission was September 1, followed by mail review, and beam time allocation by the PAC.
- The first cycle of instrument time for the CNRF as a National Facility will begin in November 1991.

Two workshops were held during this reporting period. In May, the University of Minnesota's Center for Interfacial Engineering (an NSF Engineering Research Center collaboration involving some 30 affiliate companies) conducted with NIST staff a workshop to familiarize CIE researchers with neutron techniques for interfacial applications. Ten CIE affiliate companies participated. In June, over

150 scientists from academia, industry, and government laboratories attended the Workshop on Applications of Cold Neutron Spectroscopy in Chemistry, Biology, and Physics, conducted by RRD. The purpose of the meeting was to explore some of the exciting new opportunities which will be made available to U.S. researchers when six new high-resolution inelastic scattering spectrometers are completed at the CNRF. The attendees represented 55 U.S. universities, industrial, and government laboratories, and included 13 representatives from foreign countries. Presentations made by invited lecturers gave overviews of the principles and practice of neutron spectroscopy, and the wide range of science that has been done and is being done with cold neutron spectrometers.

Following the workshop, a one-day Researchers' Group meeting was held. About 65 scientists were in attendance, of whom 47 were from institutions other than NIST. The formal part of the meeting consisted of a status report on the neutron beam facilities and detailed technical presentations on experimental stations by NIST scientists. Many important issues were

discussed which should help NIST to better meet the needs of the multidisciplinary science and engineering community which will perform research at the CNRF.

Relating to instrument development, the following collaboration was initiated in this period. The Department of Physics and Astronomy at the Johns Hopkins University has agreed to participate in the development of a cold neutron inelastic scattering spectrometer for materials research in the areas of condensed matter physics, and magnetic materials characterization, including heavy fermion systems. Johns Hopkins joins the NSF, Exxon, the University of Minnesota, IBM, Sandia National Lab, and NIST as PRT members for CNRF instruments.

In April the third issue of the *Neutron Standard*, the RRD and CNRF newsletter, was printed and sent to approximately 2500 scientists and engineers from specialties which the CNRF could benefit. Over 1300 positive responses expressing interest have been returned by *Neutron Standards* recipients.

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## THE CHRNS-SANS INSTRUMENT AT NIST

B. Hammouda, C. Glinka, S. Krueger, C. H. Chen, J. Moyer, and W. E. Dickerson

The 30 m Center for High Resolution Neutron Scattering (CHRNS)-Small Angle Neutron Scattering (SANS) instrument has many similarities with the NIST/EXXON/ University of Minnesota (UofMN) 30 m SANS that has been in operation since April 1991. The CHRNS-SANS, however, uses a single high data rate detector of the ILL-type in a slightly different vacuum flight path that enables the detector to approach within 1.2 m of the sample. This results in an instrument that is simpler to construct and use, and which has a Q-range that is nearly as wide (0.01 to 6 nm<sup>-1</sup> compared to 0.01 to 10 nm<sup>-1</sup> for the NIST/EXXON/UofMN SANS). A schematic of the CHRNS-SANS instrument is attached (fig. 1), and a brief description of its characteristics is included in

table 1. Construction of the 30 m CHRNS-SANS instrument is now about 90% complete. It will operate on a dedicated neutron guide, NG-3, that is scheduled for installation this winter (1991-1992). The CHRNS-SANS instrument will be completed and operational by the end of 1991.

A set of user friendly SANS software packages have been developed at NIST for data acquisition and instrument control on the two new 30 m SANS instruments as well as on the old 8 m SANS instrument. These consist of: (1) a screen management system that provides a menu driven user environment for data acquisition, (2) a set of computer programs that control the data acquisition hardware which uses CAMAC modules with Direct Memory Access

## FACILITIES, OPERATIONS, AND TECHNIQUE DEVELOPMENT

to a Vax-3400 computer, (3) a software package that controls the various instrument motors through an RS232 interface, (4) a graphics software that allows for online imaging of the data, and (5) a set of data treatment programs

for the reduction and preliminary analysis of the data on the Vax-3400 computer. The ability for the users to take reduced data back home on IBM-PC and Macintosh diskettes is being provided.

CHRS 30 METER SANS INSTRUMENT

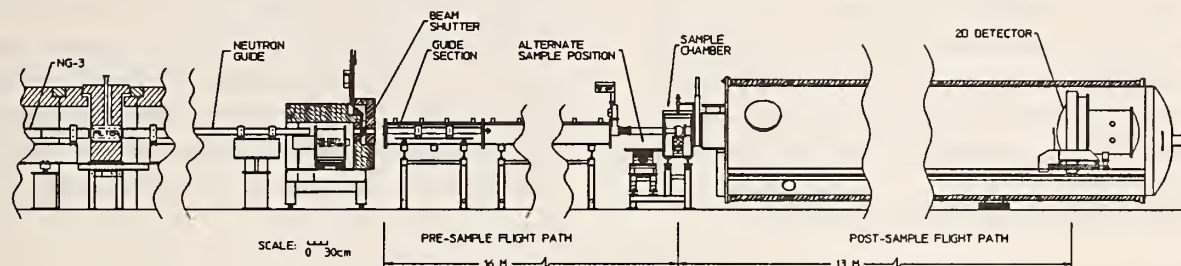


Figure 1. Schematic of the CHRS-SANS instrument

Table 1. Main characteristics of the CHRS-SANS instrument

Source Size:	6 cm x 6 cm
Wavelength Range: (velocity selector)	0.4 nm - 2.0 nm
Wavelength Resolution: (continuously tunable)	7% - 30%
Q-Range:	$0.01 \text{ nm}^{-1} - 6 \text{ nm}^{-1}$
Sample size:	0.5 - 2.5 cm
Expected Flux at sample:	$10^3$ to $10^6 \text{ cm}^{-2}\text{s}^{-1}$ depending on sample-detector distance and wavelength

## THE 30 METER NIST/EXXON/UNIVERSITY OF MINNESOTA SMALL ANGLE SCATTERING INSTRUMENT

C. J. Glinka, J. G. Barker, B. Hammouda, S. T. Krueger, J. J. Moyer,  
A. E. Heald, W. Dickerson, and C. H. Chen  
and

M. Y. Lin (Exxon Research and Engineering Co., Annandale, NJ)

The CNRF's second SANS instrument, a 30 m long, high resolution instrument developed jointly by NIST, Exxon Research and Engineering Company, and the University of Minnesota is now in operation in the guide hall at NG-7. The instrument was officially commissioned by representatives of the three institutions at a brief ceremony held at the CNRF on May 10, 1991.

This instrument extends the measurement range of the 8 m SANS instrument it

complements by nearly a factor of five and, in addition, offers a wide range of measurement conditions whereby the resolution and beam intensity can be varied to meet the requirements of an experiment. A rotating helical channel velocity selector with variable speed and pitch provides the capability to vary both the wavelength and wavelength resolution of the incident neutron beam over a wide range. Incorporated in the instrument's 15 m pre-sample

## FACILITIES, OPERATIONS, AND TECHNIQUE DEVELOPMENT

flight path are eight 1.5 m long neutron guide sections that can be easily shifted in or out of the beam to vary the beam divergence and flux on the sample by changing the effective source-to-sample distance from 3.0 to 15 m in 1.5 m increments.

To provide an exceptionally wide measurement range, the instrument's 15 m post-sample vacuum flight path has been constructed to house two large 2-d detectors; a primary detector that moves axially within the cylindrical portion of the flight path, and a second detector that moves along a circular arc (over a 40° range) at a fixed distance of 2 m from the sample. A layout of the instrument is shown in figure 1 and its characteristics are summarized in table 1. A

comparison of the neutron intensity at the sample (for a 1.5 cm diam sample and wavelength resolution  $\Delta\lambda/\lambda = 25\%$ ) versus minimum accessible Q-value for the 8 m and 30 m SANS instruments is shown in figure 2.

The instrument is presently operating with only its primary detector; the wide-angle detector will be installed in 1992. Meanwhile, development work continues on two novel components for this instrument, which if successful will significantly expand its measurement capabilities. These are a Fe/Si supermirror array for polarizing the incident beam, and a double curved, grazing incidence mirror (discussed on p. 169 in this report) to increase the flux on the sample.

**Table 1.** 30 m SANS: Instrument characteristics and performance

Source:	neutron guide (NG-7), $5 \times 5 \text{ cm}^2$	
Monochromator:	mechanical velocity selector with variable speed and pitch	
Wavelength Range:	0.5 to 2.0 nm	
Wavelength Resolution:	10% to 30% $\Delta\lambda/\lambda$ (FWHM)	
Source-to-Sample Distance:	3.0 to 15 m in 1.5 m steps via insertion of neutron guide segments	
Sample-to-Detector Distance:	primary detector - 3.5 to 15 m wide-angle detector* - 2 m (fixed), angular range from 0° to 40°	
Collimation:	circular pinhole collimation	
Sample Size:	0.5 to 2.5 cm diam	
Q-range:	primary detector - $0.01$ to $2.5 \text{ nm}^{-1}$ wide-angle detector* - $0.5$ to $10.0 \text{ nm}^{-1}$	
Size Regime:	0.5 to 500 nm	
Detectors:	$65 \times 65 \text{ cm}^2$ $^3\text{He}$ position-sensitive proportional counters ( $1 \text{ cm}^2$ resolution)	
Ancillary Equipment:	<ul style="list-style-type: none"> <li>- automatic multi-specimen sample changer with temperature control from -10 to 200 C</li> <li>- electromagnet (0 to 1.5 Tesla)</li> <li>- couette type shearing cell</li> </ul>	
Neutrons on Sample vs. $Q_{\min}$	$Q_{\min}(\text{nm}^{-1})$	$I_s^a \text{ (n/s)}$
	0.01	$2.5 \times 10^3$
	0.02	$3 \times 10^4$
	0.04	$3 \times 10^5$
	0.10	$1 \times 10^6$

\*available in late 1992

<sup>a</sup>measured with  $\Delta\lambda/\lambda = .25$ , 1.5 cm diam sample

## 30 METER SANS INSTRUMENT

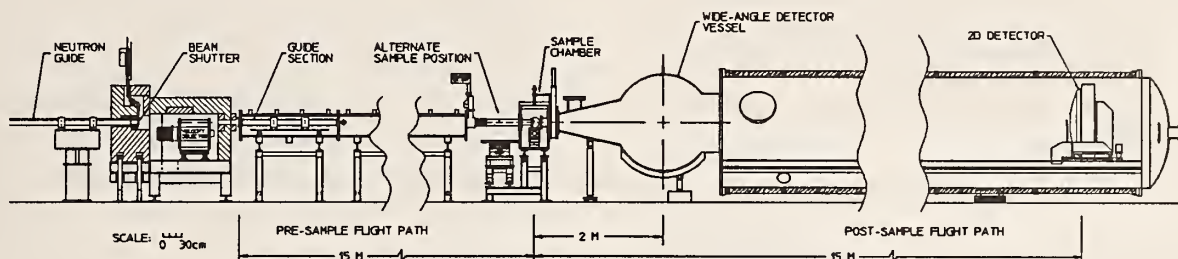
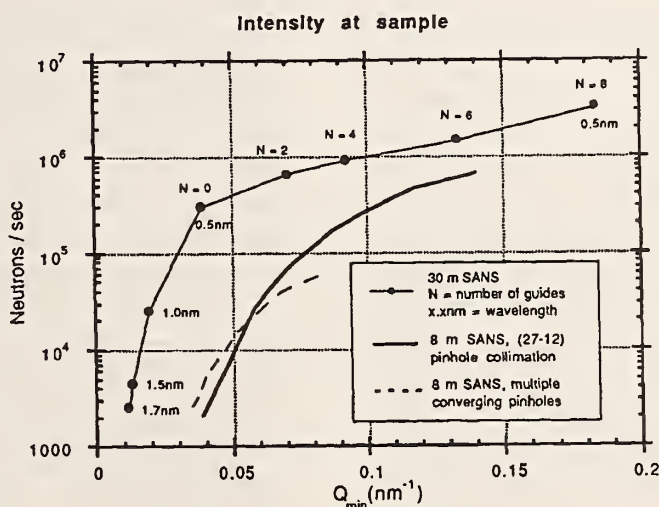


Figure 1. NIST/Exxon/University of Minnesota SANS spectrometer.

Figure 2. Comparison of neutrons/sec on a 1.5 cm diam sample versus minimum accessible Q-value for the CNRF's 8 m and 30 m (NIST/Exxon/U Minnesota) SANS instruments (for  $\Delta\lambda/\lambda = 0.25$ ).

## MULTIPLE DISK CHOPPER TIME-OF-FLIGHT SPECTROMETER

J. R. D. Copley

The chopper system for this instrument [1] comprises four vacuum housings, seven motor/bearing assemblies, seven chopper disks, and a PC-based control system. Delivery is anticipated in 1992. The design of the guide is almost complete, as is the design of masks which will limit the number of guide channels through which neutrons are permitted to pass. The detailed design of the sample chamber and detector flight path is expected to begin very soon. Prototype detectors and detector

amplifiers have been delivered and are being evaluated; we expect to place an order for a large number of detectors and amplifiers within the new few months. The instrument computer has also been ordered. Our work on the transmission properties of a separated pair of counter-rotating choppers [2] has been published [3], and an overall review of the project was presented at the International Conference on Neutron Scattering in Oxford in August 1991.

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## COLD NEUTRON DEPTH PROFILING

G. P. Lamaze, R. G. Downing, J. K. Langland (Nuclear Methods Group)  
and

S. T. Hwang (KSRI, Taedok Science Town, Taejon, Korea)

The Cold Neutron Depth Profiling (CNDP) facility at Cold Tube West (CTW) became operational on October 31, 1990. The neutron beam is filtered by 13.5 cm of single crystal sapphire which has the effect of reducing the slow neutron fluence rate by 1/3, but the fast neutron fluence rate by a factor of about 500. Collimators are located both within the biological shield and in the external-to-the-shield rotating shutter. The shutter is two cylinders, whose beam tubes fully align in the beam open configuration and are nonaligned in the beam closed configuration to reduce streaming. The collimators in these shutters can be accessed in the beam closed configuration with the reactor at full power. The diameter and intensity of the neutron beam can then be modified at any time to suit the needs of a particular experiment. The measured neutron fluence rate (capture flux) at the target position with the 16 mm diam collimator is  $1.2 \times 10^9 \text{ cm}^{-2}\text{s}^{-1}$ . A pancake fission chamber mounted on the entrance port of the NDP chamber provides a run-to-run monitor.

The target chamber was obtained from a commercial vendor using a design developed at NIST. The entire chamber is stainless steel and uses copper gaskets at all but three sealing surfaces: the beam entrance and exit windows and the opening used for changing samples. This last surface can use either viton o-rings or copper gaskets. In practice, the desire to quickly change samples usually outweighs the need for ultra high vacuum, but that capability does exist. The chamber itself is a 61 cm diam cylinder with access ports in the top and bottom

plates as well as through the side walls. All flanges conform to standard Conflat flange specifications. The standardized flanges will allow new features to be easily added in the future. Some of these include in-situ cleaning of samples, time-of-flight measurements, heating and cooling of the sample, and cooling of the surface barrier detectors.

The beam enters and exits through 10-cm diam ports sealed with thin aluminum windows. These can be replaced with sapphire windows if a metal gasket seal is required. The chamber is evacuated with a 180 l/s magnetic bearing turbo molecular pump. This pump was chosen to reduce microphonic effects on the charged particle detectors. The detectors are surface barrier detectors in a ring mount. A rotary base positions the charged particle detectors about the axis of the sample. Detectors can be placed at any angle and detectors can be mounted every 10 degrees. Currently, there exists electronics to operate four detectors simultaneously.

Samples (up to 15 cm in diam) are mounted on a set of motor driven positioners. A rotary base selects the angle of the sample with respect to the beam. The ability to rotate the detectors and sample independently allows the detector to be positioned at any angle with respect to the sample without putting the detector in the beam. Mounted on top of the sample rotator are x and y positioners. These have 15 cm of travel each, allowing a full scan of 15 cm diam samples. All four positioning devices are controlled by a PC compatible microcomputer. A program has been written in BASIC to enable unattended sample

scans. The signals from the surface barrier detectors are processed in a standard fashion and the amplified signals are sent to Analog-to-Digital converters interfaced with a multiuser minicomputer. This computer can simultaneously process data from both the thermal and cold NDP facilities. Spectra from these computers can then be transferred to a variety of other computers for data reduction, plotting, etc.

Figure 1 shows a sample spectrum taken at the cold NDP facility. The sample of Cobalt-Nickel Oxide ( $^{17}\text{O}$  enriched) was prepared by Eastman Kodak. To our knowledge, this is the first nondestructive determination of near-surface oxygen made by NDP anywhere in the world. The ability to obtain oxygen profiles is a significant addition to the elements that are now analyzed routinely at NIST: boron, lithium, nitrogen, and helium.

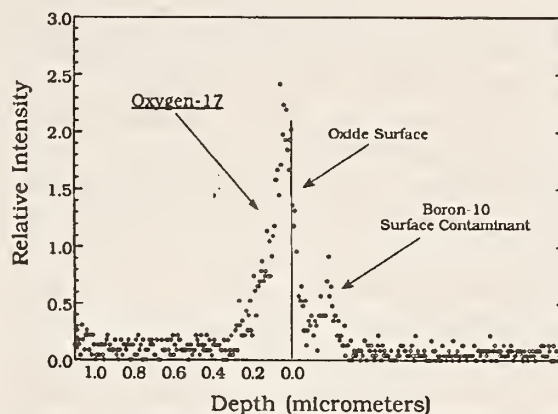


Figure 1. Neutron Depth Profile of  $^{17}\text{O}$  sample in metal oxide.

## PROMPT-GAMMA ACTIVATION ANALYSIS WITH COLD NEUTRONS

R. M. Lindstrom (Inorganic Analytical Research Division)

A permanent, full-time instrument for prompt-gamma activation analysis (PGAA) is being constructed as part of the Cold Neutron Research Facility. As a result of a compact sample-detector geometry, the sensitivity (counting rate per gram of analyte) is a factor of four better than the existing Maryland-NIST instrument. Hydrogen backgrounds of a few tens of micrograms have already been achieved, which promises to be of value in numerous applications where quantitative nondestructive analysis of small quantities of hydrogen in materials is necessary. Further reduction by one to two orders of magnitude is probable in the near future.

Experience gained in more than a decade's operation of the Maryland-NIST thermal instrument, and with cold neutrons at the German research center in Jülich, has been incorporated in the design of the instrument at the CNRF, to give high gamma detection efficiency, low background (particularly for hydrogen), and facile operation. The instrument

is installed on neutron guide NG-7 in the CNRF hall. A filter of 152 mm of single-crystal Bi and 127 mm of Be, both at liquid nitrogen temperature, is installed in the guide 3.1 m upstream from the PGAA sample position.

The apparatus is simple: the lower 50 x 45 mm of the 50 x 110 mm NG-7 guide is extracted into air through a window of magnesium 0.25 mm thick. (The upper 50 x 50 mm beam continues past the PGAA station another 2 m to the velocity selector of the 30-m SANS instrument.) A translating shutter of  $^6\text{Li}$  glass 15 mm thick just behind the window admits the neutrons to the sample. The 10-mm thick glass slab which forms the bottom of the continuing guide is capped with 15 mm of  $^6\text{Li}$  glass to avoid background from neutron scattering and capture. The neutron fluence rate was measured with 25  $\mu\text{m}$  Au to be  $1.5 \times 10^8 \text{ cm}^{-2}\text{s}^{-1}$  (thermal equivalent: using  $\sigma = \sigma_{\text{th}} = 98.65 \text{ b}$ ) at a reactor power of 20 MW.

The 1-m section of neutron guide adjacent to the PGAA station is made of boron-free

silicate glass in order to avoid generating large amounts of  $^{10}\text{B}$  capture gamma radiation from neutron leakage due to imperfections and misalignment in the guide. The outside of this guide section will be covered with a material high in  $^6\text{Li}$  and low in  $\text{H}$ , such as  $^6\text{LiF}$ -graphite paint. A plate of fused  $^6\text{Li}_2\text{CO}_3$  with a 20-mm aperture, placed just behind the shutter, collimates the neutron beam to a size not much larger than a typical sample. A beam stop of  $^6\text{Li}$  glass is placed behind the sample. Because of the purity of the neutron beam, shielding requirements are modest and scatter-capture background is low. Secondary fast neutrons generated in the collimator and beam stop by reactions of the fast tritons from  $^6\text{Li}(\text{n}, \alpha)^3\text{H}$  have not yet been troublesome. Hydrogen-containing materials have been avoided to the maximum extent possible in the vicinity of the sample and detector. Samples are held in the beam in envelopes of 25- $\mu\text{m}$  Teflon FEP between the prongs of a supporting fork. The volume between the neutron collimator and the beam stop assembly can be flooded with He at atmospheric pressure in a Teflon tent to reduce air scatter.

A Ge gamma-ray detector (27% relative efficiency, 1.7 keV resolution) views the sample through a  $^6\text{Li}$ -glass window along an axis at right angles to the neutron beam. The field of view of the detector is collimated so as to view the sample. Environmental gamma radiation is reduced by shielding the detector with at least 100 mm of lead in all directions. The lead in turn is shielded from stray neutrons (which produce 7-MeV Pb capture gamma rays) with sheets of Boral. The detector shield rests on a table, the top of which is adjustable vertically and parallel to the beam with leadscrews. The table rolls on a track perpendicular to the beam to adjust the counting distance, which can be as close as 200 mm from the sample to the front face of the detector. Experiments are continually under way to optimize the shielding in the vicinity of the sample-detector assembly.

Gamma-ray spectra are acquired with a 16384-channel analog-digital converter coupled to a multichannel pulse height analyzer (ND556 AIM). The AIM is controlled over the building-wide Ethernet by Nuclear Data acquisition and display software on a VAXstation 3100.

Several measurements have been made in the short time that this cold-neutron instrument has been in operation. Sensitivities of a number of elements were compared with those of the thermal Maryland-NIST PGAA instrument. At the same reactor power, sensitivities for most elements are a factor of four to six better with the cold-neutron apparatus than with the thermal instrument.

The first measurement with cold neutron PGAA in the CNRF was the determination of hydrogen in a sample of  $\text{C}_{60}$  fullerene "buckyballs" intended for neutron scattering studies. Cold-neutron PGAA found a hydrogen concentration of  $0.92 \pm 0.09$  wt %, which was too high for satisfactory scattering measurements. After repurification of the material, hydrogen was measured again. A 600-mg sample, contained in the aluminum sample holder intended for the scattering measurements, was irradiated in the PGAA beam for 100 minutes live time while surrounded with a flowing atmosphere of He contained in a Teflon tent. A clear H peak was visible at more than ten times the intensity of a blank sample of spectroscopic grade graphite. The sample was found to contain  $0.077 \pm 0.014$  wt % H, which was adequately low for the neutron scattering measurements. In other work, hydrogen was measured in a  $\text{Pr}_2\text{CuO}_4$  superconductor analog; a 1-hr irradiation gave a concentration of  $[\text{H}] = 0.017 \pm 0.010$  wt %. Hydrogen was sought in a 50-nm borophosphosilicate glass film on a quarter of a 10-cm silicon wafer; an upper limit of 2  $\mu\text{g}/\text{cm}^2$  was found.

Future enhancements to the counting system will include a Compton suppressor, an automatic sample changer, and a second detector system which will permit  $\gamma$ - $\gamma$  coincidence measurements. The difficulties associated with working adjacent to the upper guide—restricted space and Si capture background—may be ameliorated in the future by deflecting the PGAA beam away from the guide. Additional improvement in sensitivity is possible since neutron optics may be used to focus cold neutrons onto a small area. Gains of an order of magnitude in fluence rate may be obtainable.

## PRELIMINARY DESIGN OF THE LIQUID HYDROGEN COLD NEUTRON SOURCE

P. Kopetka, J. M. Rowe, and R. E. Williams

A liquid hydrogen cold neutron source has been designed to replace the heavy ice cold neutron moderator chamber now in use. While a final choice of the  $\text{LH}_2$  chamber geometry has yet to be made, a 3 to 5 liter vessel will be positioned as close as possible to the reactor core. Major features of the system are independent of this choice, however, and a preliminary safety analysis report has been prepared and distributed locally. The design philosophy is to install a simple, passively-safe system, with multiple barriers preventing oxygen from mixing with hydrogen.

**Source Geometry.** Until very recently, the choice for the  $\text{LH}_2$  moderator was two rows of vertical tubes, 30-cm tall and with 1.6-cm radii, as shown in figure 1. With seven tubes facing the neutron guides, the source presents an area of more than  $900 \text{ cm}^2$ . A large area is needed to fully illuminate the guides because their point of intersection is located about 25 cm in front of the source. Monte Carlo neutron transport calculations using MCNP indicate gains of a factor of 2 to 3 over the existing source for

wavelengths greater than 4 Å. Approximately 2.5 L of  $\text{LH}_2$  at 20 K and 1.5 atmospheres will fill the tubes, assuming a density of  $0.056 \text{ g/cm}^3$ , corresponding to a 20% void fraction. Liquid hydrogen would be delivered to the bottoms of the tubes through 13 lines from a liquid manifold, and the vapor from the tops of the tubes returned via 13 lines to a gas manifold. The manifolds are connected to the hydrogen condenser, completing a thermosiphon. The bismuth tip surrounding the existing source will be removed, allowing the new source to be located much closer to the core than the heavy ice. The tubes would be mounted in an insulating vacuum, which will be surrounded by a He-filled containment. The cryostat shell will be cooled by a layer of  $\text{D}_2\text{O}$ .

Recent MCNP results have shown a chamber in the shape of either a spherical shell or a cylindrical annulus will produce substantially higher yields of long wavelength neutrons than the tube source. The voids in the centers of these sources act as cold-neutron flux traps, as demonstrated by the performance of the new

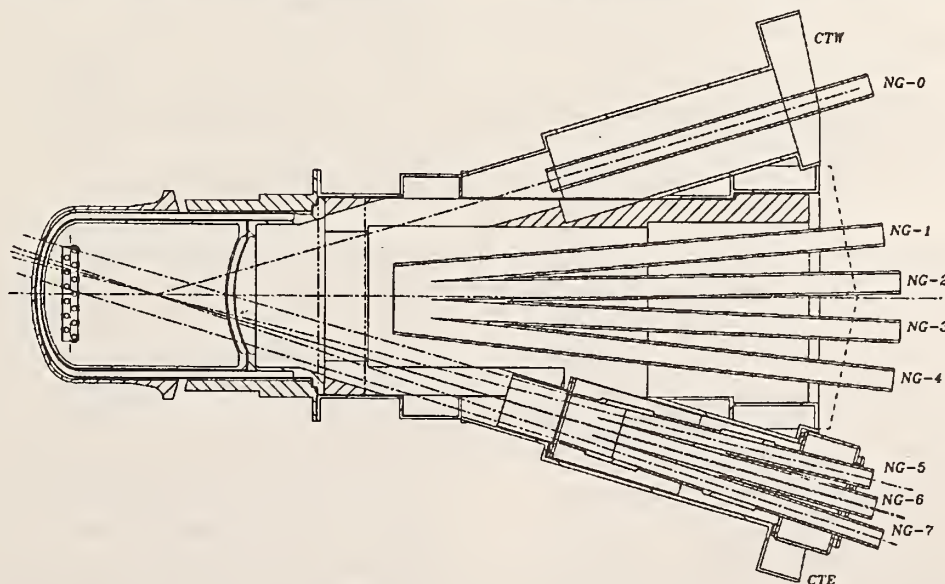


Figure 1. Plan view of a liquid hydrogen cold neutron source consisting of 13 vertical tubes.

cylindrical  $\text{LH}_2$  cold source at the Orphée reactor in Saclay, France [1]. In our case, the chamber would be larger than the Saclay source, and would have a reentrant hole facing the guides. The inside chamber may have very thin walls because the void is maintained by hydrogen vapor trapped inside. Most of the heat is generated in the outer wall. Liquid is introduced at the top of the inner (cool) wall, flowing downward by gravity to the chamber bottom, thus establishing a naturally circulating loop, with vapor exiting at the top. An effort is now underway to model the boiling heat transfer in these sources, and to optimize the shape parameters for the most favorable neutronics. A shell type source would require 4 to 5 L of  $\text{LH}_2$ . It would be mounted in an insulating vacuum identical to that described above.

**System Description.** A schematic diagram of the system is shown in figure 2. The choice of moderator geometry has very little impact on the rest of the system, which is designed to be as safe and simple as possible. The hydrogen system is a closed loop thermosiphon with no moving parts. There will be a minimum of gas handling because once the system is charged

with hydrogen, it need not be reopened except to repair a major failure. A series of large ballast tanks, always open to the  $\text{LH}_2$  chamber, insure low system pressures in the event of refrigerator failure and vaporization of the entire  $\text{LH}_2$  inventory. The ballast volume will be chosen so the maximum pressure will be 3 to 5 atmospheres. A large fraction of the  $\text{H}_2$  inventory will be liquified while the cold source is operating, as the cold operating pressure will be 0.6 to 1.5 atmospheres.

A naturally circulating loop will be established as the hydrogen vapor produced in the moderator chamber rises to the condenser, is liquified, and flows by gravity back to the chamber. Such thermosiphons, requiring no pumps or blowers, are being used at Saclay and the ILL reactor in Grenoble. The condenser, located outside of the reactor biological shield, will be cooled by He gas at 18 K provided by the 3.5-kW refrigerator now installed and in its final phase of acceptance tests.

All parts of the hydrogen system will be located to minimize the possibility of accidental ruptures. The moderator chamber will be in core and out of harm's way. The condenser will

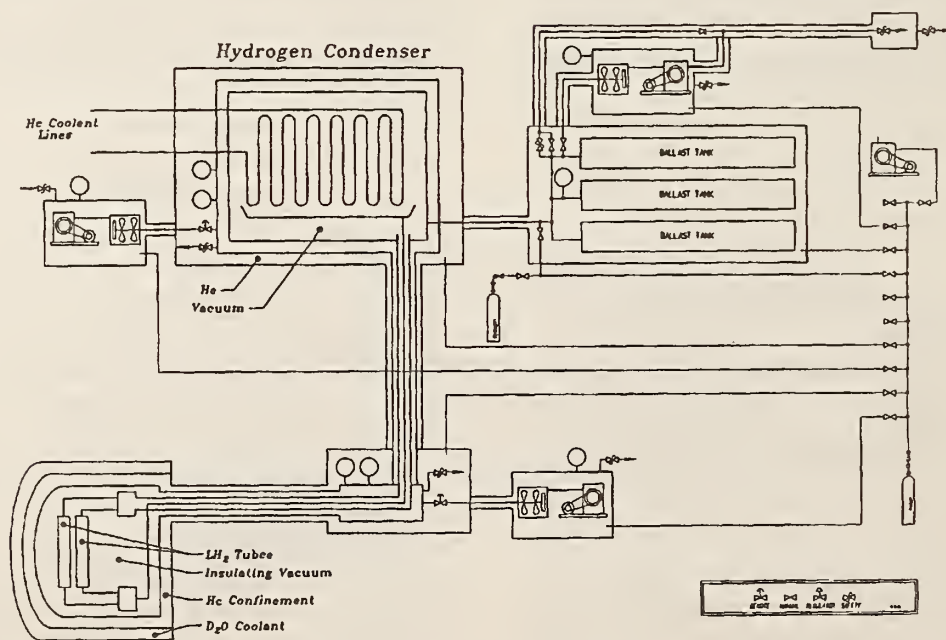


Figure 2. Cold source schematic. The moderator shown consists of vertical tubes. A different choice of moderator chamber changes only the interior of the cryostat.

## FACILITIES, OPERATIONS, AND TECHNIQUE DEVELOPMENT

be located at the face of the reactor shield, out of reach of the crane, behind a steel shroud. The ballast tanks will be mounted in the cavities on the ceiling, above the path of the crane.

Every precaution will be taken to prevent the mixing of oxygen and hydrogen. The  $H_2$  used in the system will be checked to assure a purity of 99.9995% before it is introduced to the system, and checked periodically for the presence of  $O_2$ , as will the He containment volumes. There are three barriers preventing the introduction of air into the  $LH_2$  chamber: the hydrogen volume boundary, the insulating vacuum, and the He containment volume, maintained at 2 psi above atmospheric pressure. System pressures are constantly monitored for evidence of leaks. The existing heavy ice source has such a triple containment scheme. The warm hydrogen components are also surrounded by He containment volumes so leaks may be detected before mixing with air can occur.

Safety Analysis. Although the cold source is designed to minimize the probability of mixing hydrogen and oxygen, it is necessary to analyze the effects of accidents resulting from system failures. There has been a great deal of research on hydrogen deflagration and detonation, making possible such an accident analysis. Results indicate:

- (1) Overpressure due to  $LH_2$ -solid  $O_2$  reactions will not exceed the working pressure of the hydrogen system.
- (2) Detonation of the  $H_2$  inventory in room C-100 will not result in structural damage in an unconfined vapor phase explosion.
- (3) A catastrophic rupture of the lines to the cryostat vacuum chamber, followed by a release of  $H_2$  into this volume containing condensed  $O_2$  and subsequent detonation, will not exceed the bursting pressure of the vacuum chamber.
- (4) The detonation of a stoichiometric air-hydrogen mixture in the moderator will not rupture the hydrogen container.

No credible accident can result in damage to the reactor or breach the confinement boundary.

The Safety Analysis Report will be completed this fall, as decisions are made regarding the moderator chamber geometry. The new cold source is expected to be ready for installation at the same time as the installation of the remaining neutron guides.

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## DEVELOPMENT OF A FOCUSING MIRROR FOR SANS

J. G. Barker, C. J. Glinka, C. F. Majkrzak, and S. K. Satija

The high resolution small angle scattering spectrometer will use a doubly curved grazing incidence mirror described in ref. [1]. Before coating the cylindrical mirror sections, scattering measurements were made on additional test mirror surfaces to determine whether the amount of nonspecular scattering produced by the mirror surface roughness is tolerable. Measurements were made on one of the cylindrical quartz sections to be actually used in the focussing mirror construction, on nickel coated and uncoated sections of a Borkron glass, and on a nickel coated float glass. Optical profilometry results indicate that all the surfaces have similar mean roughness,  $\sigma_{rms} \approx 0.4\text{-}0.6$  nm.

The measurements were made on the 8 m SANS instrument in a configuration that allowed the scattering (specular plus nonspecular) from the mirror specimens to be measured over nearly six orders of magnitude in intensity. The scattering was found to be concentrated perpendicular to the mirror surface. A plot of the scattering in this direction is shown in figure 1 with the scattered intensity normalized by both the beam intensity incident on the mirror and detector solid angle. The uncoated mirrors were tested at a lower incident scattering vector ( $q_i = 0.1 \text{ nm}^{-1}$ ), to achieve complete reflection.

The scattering roughly follows a power-law:  $I_{ns} \propto q^{-2}$ . Table 1 lists the surface roughness

and scattering at  $q = 0.15 \text{ nm}^{-1}$  for each mirror. The mirrors have similar mean roughness but exhibit an order magnitude difference in scattering at small angles. This indicates that the distribution of the surface roughness is as important as the mean roughness in determining the magnitude of nonspecular scattering at small angles. Previous X-ray measurements on mirror surfaces indicate that the surface roughness correlation function can be approximated by an exponential distribution [2]. According to the Kirchhoff approximation [2], the nonspecular scattering at angles large compared to the angle of incidence follows the observed law:  $I_{\text{ns}} \propto q^{-2}$ .

The background from the uncoated cylindrical mirror is considered satisfactory for the current application. Before coating the mirrors, further testing is being conducted to improve the coatings. The 30-m SANS spectrometer will extend the present measurements to smaller angles designed for the focussing mirror ( $q \approx 0.01 \text{ nm}^{-1}$ ).

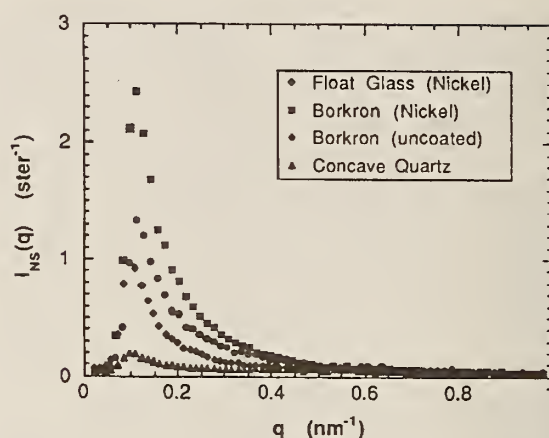


Figure 1. Plot of the measured nonspecular scattering as a function of  $q$  for different mirror surfaces.

Table 1. Mean surface roughness and measured background scattering at  $q = 0.15 \text{ nm}^{-1}$

Mirror	$\sigma_{\text{rms}}$	$q_i$	$I_{\text{ns}}(q=0.15 \text{ nm}^{-1})$
Ni Coated Float Glass	~	$0.15 \text{ nm}^{-1}$	$0.9 \text{ ster}^{-1}$
Ni Coated Borkron	0.45 nm	0.15	1.45
Uncoated Borkron	0.55	0.10	0.54
Uncoated Concave Quartz	0.55	0.10	0.12

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TRANSMISSION PROPERTIES OF CURVED-STRAIGHT  
NEUTRON GUIDE SYSTEMS

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and

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Curved neutron guides are often used to reduce fast neutron and gamma ray background. They have the inherent disadvantage that the transmitted neutron intensity distribution is spatially asymmetric; this asymmetry, which depends in part on the dimensions of the guide, is particularly pronounced at short wavelengths. The idea of adding a straight section of guide at the end of a curved guide has been suggested [1] as a method to reduce this asymmetry and to make the beam more uniform. We have examined [2] the behavior of neutron trajectories within curved-straight neutron guide systems, using both ray-tracing and analytical approaches to the problem. Trajectories which correspond to neutrons transmitted by the curved guide [3] are used as input for the straight guide calculations, and distributions are determined as a function of the length of the straight guide.

We have described the construction of the acceptance diagram at the exit of a straight guide of arbitrary length  $L$  following a curved guide which is at least as long as the line-of-sight length,  $L_c$ . The acceptance diagram at the exit of the curved guide is bounded by a parabola which depends on the critical angle  $\theta_c$  of the guide surface (and therefore on the neutron wavelength), and on the characteristic angle  $\psi_c$  of the curved guide (and therefore on the guide dimensions). In the absence of the straight guide, the acceptance diagram at a distance  $L$  from the curved guide has shifted in phase space, and is bounded by a similar parabola, though its vertex is shifted. Using the method of rotation of acceptance diagrams [4], we have constructed the phase diagram at the exit of a straight guide of arbitrary length.

The characteristic angle or wavelength of the curved guide determines properties such as the spatial intensity distribution function  $N(z)$ , which represents the intensity at position  $z$  within the guide, integrated over the angular variable  $\psi$ . This function changes as neutrons

propagate down the straight guide. Examples are shown in figure 1. At the entrance of the straight guide  $N(z)$  is a parabolic function but its form becomes more complicated as  $L$  is increased. The intensity tends to slosh from one side of the guide to the other as neutrons proceed down the guide, like water in a bath tub, and this transverse wave dampens out with increasing  $L$ . At sufficiently large distances it tends to the constant value  $N_0$ . We find that neutrons of a given wavelength  $\lambda$  move through the straight guide in such a way that the distribution is both better centered and more uniform at some locations than at others further downstream.

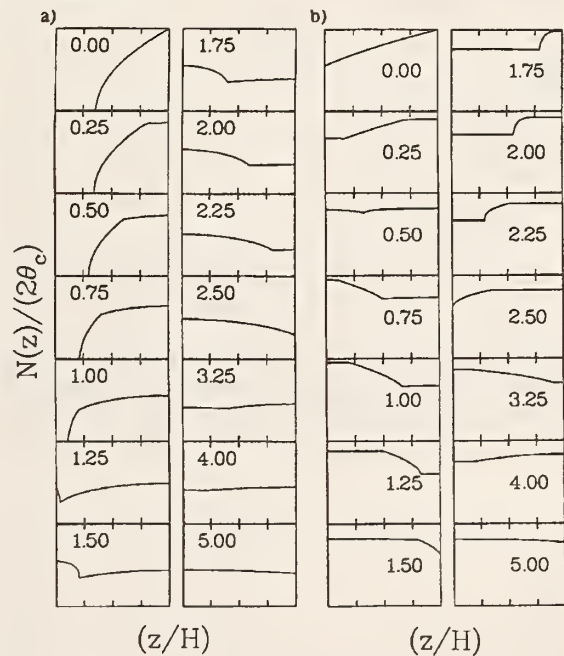


Figure 1.  $N(z)/2\theta_c$  for  $\xi = \theta_c/\psi_c$  equal to (a) 0.8 and (b) 1.2, for values of  $(\psi_c/\psi_0)$ , indicated on the plots, from 0 to 5.

The straight guide length  $L$  is characterized by the angle  $\psi_0 = H/L$  where  $H$  is the width of the guide. We use two parameters to characterize the spatial distribution  $N(z)$ : the normalized first moment  $\langle z \rangle / H$ , or effective center of the distribution, and the normalized standard

deviation  $\sigma_N/N_0$  which is a measure of the uniformity of the beam. Values of these quantities are shown in figure 2 as a function of  $\psi_c/\psi_0$  (which is proportional to  $L$ ), for different values of  $\xi = \theta_c/\psi_c$  (which is proportional to  $\lambda$ ).

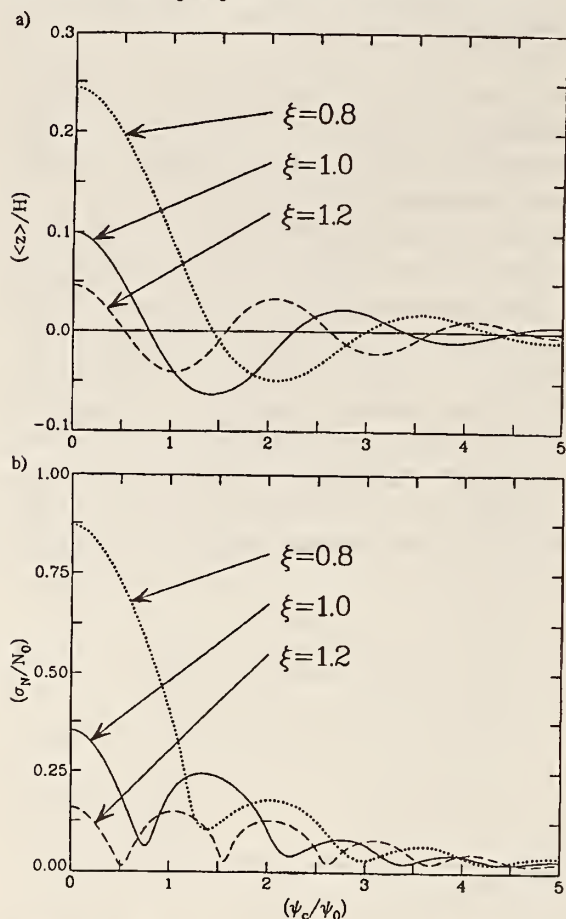


Figure 2. (a) The normalized first moment  $\langle z \rangle/H$ , and (b) the normalized standard deviation  $\sigma_N/N_0$ , plotted as functions of  $\psi_c/\psi_0$ , for three different values of  $\xi = \theta_c/\psi_c$ .

For increasing straight guide length  $L$ , the first moment oscillates about zero with decreasing amplitude, indicating that the intensity distribution is becoming better centered. The asymmetry and non-uniformity introduced by the curved guide, though more pronounced at wavelengths less than the characteristic wavelength of the guide, dampen out more rapidly as a function of straight guide length than in the case of neutrons of longer wavelength. The distance between successive nodes becomes shorter at longer wavelengths. There is a correlation between the positions of the nodes of  $\langle z \rangle/H$  and the positions of the minima in  $\sigma_N/N_0$ . The standard deviation dampens more rapidly for shorter wavelengths, though the distance between successive extrema is greater.

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## TRANSMISSION OF NEUTRON BENDERS

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and

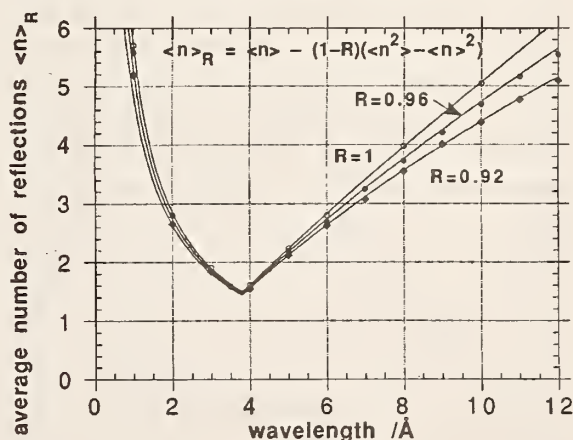
A. A. van Well and V. O. de Haan (Interfacultair Reactor Instituut, Delft, Netherlands)

Beam benders and curved guides can be used on neutron guide systems for steering the beam over short distances, and for increasing the number of desirable end positions; they can also be used as devices on neutron optical systems, such as stacked microguides for neutron focusing. Analytic expressions are available for the transmission of the bender with no reflectivity losses and the average number of both garland and zigzag reflections for trajectories through a curved guide as a function of wavelength [1]. Expressions are obtained for cases where the concave and convex surfaces of the guide have the same and different coatings respectively. We assume complete illumination of the guide, and that the coefficient of reflection is unity for all surfaces up to their critical angle. Since the grazing angle at the concave surface for zigzag reflections is always greater than that at the convex surface, the convex surface may have a smaller value of the critical angle than that of the concave surface.

Approximate analytic expressions for determining the transmission of neutron benders which take into account reflectivity losses using the mean number of reflections agree well [2] with computer simulation results which track the neutron trajectories directly, provided that the reflectivity  $R$  is high. The transmission for a particular trajectory must be modified by a factor  $R^n$  where  $n$  is the number of reflections for that trajectory. In the computer simulation all possible successful trajectories at a particular wavelength must be sampled randomly, so that the simulation should perform an average  $\langle R^n \rangle$ , where  $\langle \dots \rangle$  indicates an average over all trajectories at a given wavelength. The average number of reflections applied as a reflectivity correction  $R \langle n \rangle$  to the transmission curve for the bender agrees well with the simulation results. This approximation is valid

provided that the reflectivity is close to unity. The plots show, however, an increasing deviation at longer wavelengths.

Figure 1 shows the values of the mean number of reflections  $\langle n \rangle_R$  for successful trajectories through a bender of length  $L_c$  (the length necessary to eliminate lines of direct sight) obtained from the simulation for reflectivities  $R = 0.96$  and  $0.92$ . The deviation is small for garland reflections only, or  $\lambda \leq \lambda_c$ . For a given reflectivity  $R$ , the average number of reflections is approximated by  $\langle n \rangle_R \approx \langle n \rangle - (1 - R)(\langle n^2 \rangle - \langle n \rangle^2)$ . We find that this equation gives very good agreement with the data from the simulation for  $R = 0.96$  and  $0.92$  for  $\lambda > \lambda_c$ . We also find that  $\langle n^2 \rangle - \langle n \rangle^2$  may be replaced by  $\langle n \rangle^2/3$ . This is exact at  $\lambda = \lambda_c$ , and asymptotically as  $\lambda \rightarrow \infty$ , and is a good approximation elsewhere since the coefficient of the most significant term is zero.



**Figure 1.** Values of the mean number of reflections  $\langle n \rangle_R$  for successful trajectories through a bender of width  $H$  and length  $L_c = \sqrt{8H\rho}$  obtained from a computer simulation, a) assuming no reflectivity losses (open circles), and b) accounting a reflectivity  $R = 0.96$  (closed circles) and  $0.92$  (closed diamonds). Also shown by the solid lines are the mean number of reflections a)  $\langle n \rangle$  assuming no reflectivity losses, and b)  $\langle n \rangle_R = \langle n \rangle - (1 - R)(\langle n^2 \rangle - \langle n \rangle^2)$  for reflectivities  $R = 0.96$  and  $0.92$ .

The transmission of a neutron bender or curved guide with *any* value of reflectivity can be determined exactly [3] using exponential integral functions,  $E_n(x)$ . The functional form differs above and below the characteristic wavelength of the guide, and we have determined various properties of the transmission as a function of wavelength. The transmission through the bender of length  $L_c$  including reflectivity losses is given by

$$T(\lambda) = 2 (\lambda/\lambda_c)^2 E_4(y), \quad \lambda < \lambda_c$$

where  $y = (\lambda_c/\lambda) |\log R|$ , and

$$T(\lambda) = \frac{2(\lambda_c/\lambda) [E_4(x) - \{E_4(2x) - (x^*/x)^{-3} E_4(2x^*)\}/4 + \{E_0(2x) - (x^*/x) E_0(2x^*)\}/4]}{\lambda > \lambda_c}$$

where

$$x^* = |\log R| [(\lambda/\lambda_c) + \{(\lambda/\lambda_c)^2 - 1\}^{1/2}]$$

and  $x = |\log R|$ . This is shown in figure 2 for various values of reflectivities. If the bender has a length  $L$ , then the values of the functions  $y$ ,  $x$ , and  $x^*$  should be multiplied by a factor  $(L/L_c)$ .

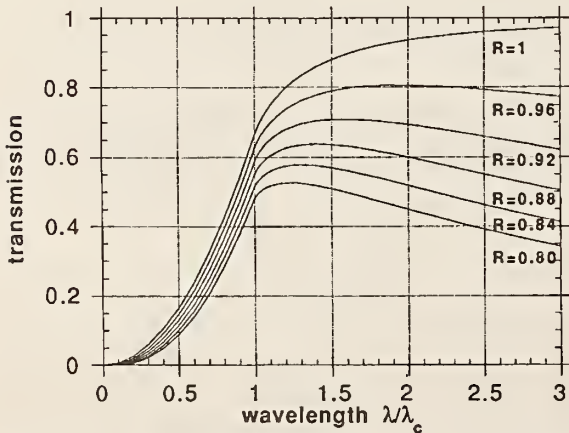


Figure 2. The transmission through a neutron bender of width  $H$  and length  $L_c = \sqrt{8H\rho}$  as a function of wavelength  $\lambda$  for various values of the reflectivity  $R$  of the surface.

The mean number of reflections has also been determined for any value of reflectivity in terms of exponential integral functions. This may be written as

$\langle n \rangle_R = |d(\log \langle R^n \rangle)/d(\log R)|$ , and is evaluated to give:

$$\langle n \rangle_R = (\lambda_c/\lambda) E_3(y)/E_4(y), \quad \lambda < \lambda_c$$

where  $y = (\lambda_c/\lambda) |\log R|$ , and

$$\langle n \rangle_R = \frac{[E_3(x) - \{E_3(2x) - (x^*/x)^{-2} E_3(2x^*)\}/2 + \{E_{-1}(2x) - (x^*/x)^2 E_{-1}(2x^*)\}/2]}{[E_4(x) - \{E_4(2x) - (x^*/x)^{-3} E_4(2x^*)\}/4 + \{E_0(2x) - (x^*/x) E_0(2x^*)\}/4]} \quad \lambda > \lambda_c$$

where

$$x^* = |\log R| [(\lambda/\lambda_c) + \{(\lambda/\lambda_c)^2 - 1\}^{1/2}]$$

and  $x = |\log R|$ .

These expressions become the same as those for the straight guide in the limit of large wavelengths. From the results, a simple approximate expression for the transmission can be obtained which has been shown useful for short benders with high reflectivity. The calculations have also been applied to the transmission for a beam bender which has different coatings on the inner and outer surfaces of the guide.

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## STUDIES ON SILICON WAFER MICROGUIDES FOR NEUTRON FOCUSING

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The concept of using bent silicon wafers as a focusing element for analytical measurements using neutron absorption techniques has been tested at CT-W. We have obtained preliminary results using nickel-coated silicon wafers as neutron microguides.

We have conducted studies of the neutron reflection properties of the 200  $\mu\text{m}$  thin single crystal silicon wafers coated on both sides with (natural isotopic) nickel. These wafers will be used to construct a microguide, where the neutrons are transmitted through the silicon and reflected by the nickel. A large number of these wafers, stacked and bent to a particular radius of curvature with an appropriate variation in the length, can be formed into a neutron lens to focus a large area beam onto a high-intensity line with a width in the millimeter range. These wafers have been characterized with x-ray reflectivity measurements at beam line X-11 B of the National Synchrotron Light Source, with x-ray wavelength of 1.74  $\text{\AA}$ . As shown in figure 1, a fit with a Fresnel model gives a thickness of the nickel coating of 700  $\text{\AA}$ , and a surface roughness of 20  $\text{\AA}$ . For the wavelengths of cold neutrons ( $\lambda > 4 \text{\AA}$ ) such roughness is negligible in terms of its effect on the reflectivity below the critical angle. However, x-ray photographs of the reflected beam show significant broadening, indicating long-range waviness of the wafers, which is well known for thin unsupported layers. In our application, the wafers are to be tightly clamped down and, more importantly, to be bent by exerting a force on one edge. Therefore, the waviness should be minimized.

The neutron measurements have been performed in conjunction with the development of the new neutron camera as a detector, which enables real-time position sensitive neutron counting. The wafers are stacked and oriented along the direction of the neutron beam.

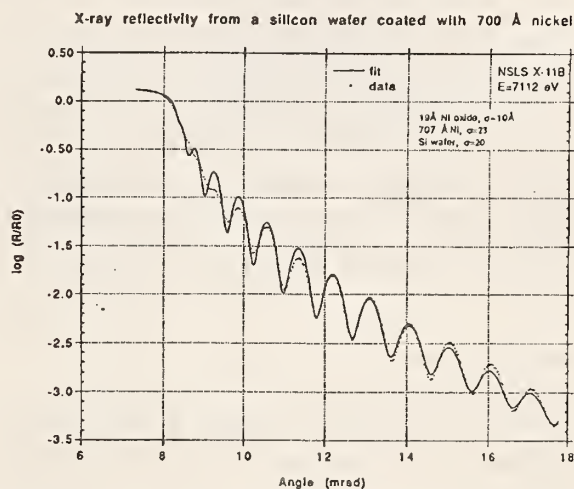
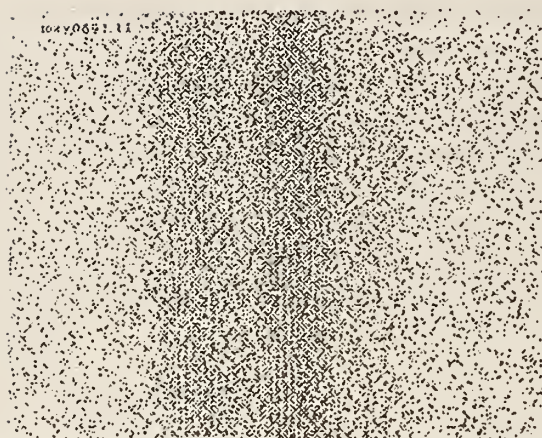
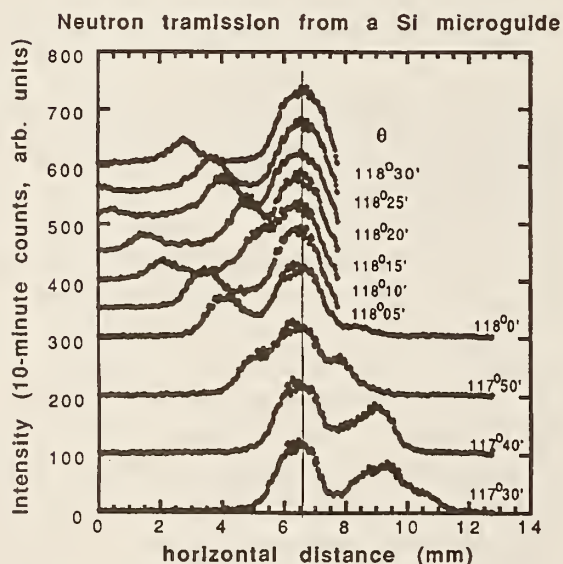


Figure 1. X-ray reflectivity measurements and fits for a 200 mm diam silicon wafer coated with 700  $\text{\AA}$  nickel. Data taken at NSLS beam line X-11B.

Pictures are taken at various angles of orientation. The guide length formed by the wafers is 2 inches (the diameter of the wafers). The neutron beam has a wavelength range from 2 to 9  $\text{\AA}$ . Those neutrons incident with an angle smaller than the critical angle of the total external reflection are reflected from the wafer surfaces at an angle of  $2\theta$  from the incident beam,  $\theta$  being the angle between the incident beam and the wafer surface. The remaining neutrons penetrate without being reflected. As shown in figure 2, two fringes are seen on the video monitor, a main peak as the straight through beam and a side peak as the reflected beam. As the incident angle  $\theta$  is varied by  $\Delta\theta$  by rotating the wafer holder, the reflected beam shifts by  $2\Delta\theta$ . This effect is shown in figure 3, where the horizontal profiles are obtained by integrating over all vertical pixel readings, displaying the intensity of the direct and reflected beams as a function of horizontal position at various incident angles. With an



**Figure 2.** Neutron beam output from a silicon microguide imaged using the new neutron camera. Both defocused (left) and direct (right) beams are imaged.



**Figure 3.** Integrated relative intensity (arbitrary units) of neutron transmission and reflection profile from a silicon microguide at various incident angles.

improved neutron sensor, further fine structure within the main peak and the reflected peak is revealed. We do not yet understand the nature of this fine structure. Similar experiments have been performed on a single wafer and equivalent results are found.

Ultimately, we wish to focus a white neutron beam for material research. However, to understand quantitatively the transmission of neutrons through nickel-coated silicon wafers

and to compare with the results of theoretical studies, it is meaningful to perform measurements with a monochromatic beam. We have mounted a stack of nickel coated silicon wafers parallel to the direction of the neutron beam at BT-7 (wavelength 2.35 Å). One of the measurements performed is a profile of the transmitted beam using three different entrance-slit widths: 1/4-, 2-, and 6 times the wafer thickness of 200 μm. The integral of the profile normalized to the direct beam gives an estimate of the transmission efficiencies, which are 0.68, 0.86, and 0.85 for the three settings, respectively.

We have also carried out cold neutron transmission measurements through the 200 μm wafers using neutrons of wavelength 7 Å on the instrument S3 at the Institut Laue-Langevin, Grenoble, France. Using a well collimated incident beam, rocking curve measurements have been conducted on straight wafers placed end-to-end and side-by-side, and on curved wafers. When the straight wafers are placed end-to-end, we observe the expected broad angular response, with a width dependent on the critical angle of the silicon-nickel interface ( $\gamma_c = 1.53 \text{ mrad-Å}^{-1}$ ), essentially independent of the number of reflections necessary for transmission. The measurements show that within the entire angular range, the measured reflection coefficient for the internal silicon-nickel interface has the value of  $0.988 \pm 0.005$ . Some measurements include up to 11 orders of reflection. The transmission measurements suggest a total removal cross section through the silicon somewhat higher than expected. The silicon wafers are undoped and prompt gamma activation analysis shows that the boron to silicon ratio is less than  $10^{-6}$  so that this cannot be accounted by the bulk boron concentration. In addition, transmission measurements have been performed on a straight wafer as a function of wavelength at different incident angles to the incident beam, on the instrument EROS at the Laboratoire Léon Brillouin, Saclay, France. As the inclination angle is increased, we observe a cut off in transmission which increases with angle, and therefore with wavelength, which agrees well with expectation.

These studies provide information on the properties of the microguide materials for the future construction of focused neutron elements.

## DEFLECTION OF NEUTRON BEAMS USING CAPILLARY OPTICS

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Low energy neutrons have optical properties analogous to those of photons. A recent development [1] in x-ray focusing using capillary optics, a device called the Kumakhov lens, has prompted us to experiment with this new approach. In principle, the capillary lens transports neutrons in the same way as the silicon wafers, except that the former provides a guide which can focus in two dimensions rather than one. Technology has enabled thousands of channels to be formed within a glass fiber of sub-millimeter diameter. These fibers are termed polycapillary fibers. The lens is formed by bending and orienting the fibers in such a way that the beams emerging from each fiber point to a small spot and so we achieve focusing.

We have observed the transmission of neutrons through bent capillaries. Each fiber has a hexagonal cross section, containing over one thousand capillaries, each capillary having an internal diameter of 6  $\mu\text{m}$ , and an external diameter of 10  $\mu\text{m}$ . We cut 30 fibers each to a length of 200 mm. These 30 fibers were laid horizontally, side by side, on a steel ruler. We placed small bar magnets across the top of the fibers to hold them flat on the ruler at one end. A positioning bar driven by a translational stage at the other end enabled us to curve the fibers up and out of the straight-through beam. Raising one end by a distance  $s$  over a length  $\ell$  (from the pivot point to the lifting point), the induced radius of curvature of  $R$  the fibers is given by  $R = \ell^2/2s$ . We raised the end of the capillaries from the straight through beam by a distance of 9 mm, and the pivot point was 150 mm from the end, giving a radius of curvature of 1.25 m.

The incoming neutron beam was defined by slits of cadmium and lithium carbonate, with the same width as the fibers. A polaroid neutron camera recorded both the direct and the guided neutron beams at different distances from the exit of the fibers. As shown in figure 1, the results demonstrate that the trajectories of neutrons are bent by their passage through curved fibers.

Another measurement has been performed by mounting the fibers vertically, and taking pictures with a specially modified CID camera at the exit, for various bending distances  $s$ . As  $s$  is increased, so that the radius of curvature  $R$  is decreased and therefore the characteristic wavelength  $\lambda_c$  is increased, the relative intensity of neutrons whose trajectories can be bent by the capillaries is decreased (fig. 2).

This measurement has been repeated on four different types of capillaries: two polycapillary fibers, one made of lead glass, the other containing boron; and two single capillary fibers, one coated with plastic protecting layer and the other without. The two polycapillary fibers appear to conduct neutrons equally well and much better than the single capillary fibers. The latter show the characteristic 'crescent' shaped output image, indicating the lower transmission efficiency caused by incomplete illumination due to the increased channel diameters. These measurements demonstrate clearly the ability to transport cold neutrons through narrow capillaries and to guide their trajectories, and will lead eventually to the focusing of neutron beams using this technique.



Figure 1. Photographs of neutron beam intensities through the capillaries. The bottom images, indicated by an arrow, are from the direct beam. The images (inclining) are from the guided beam, which is deflected through a small angle of 120 mrad. As the cameras is moved farther away, the distance between the direct beam and the guided beam becomes larger, as seen from left to right. The two photographs were taken with different entrance slit widths.

$R\text{ (m)}$	---	3.38	1.59	1.13	0.85	0.67	0.56	0.49	0.42	0.38
$\lambda_c\text{ (Å)}$	0	1.36	1.92	2.35	2.71	3.03	3.32	3.59	3.83	4.07

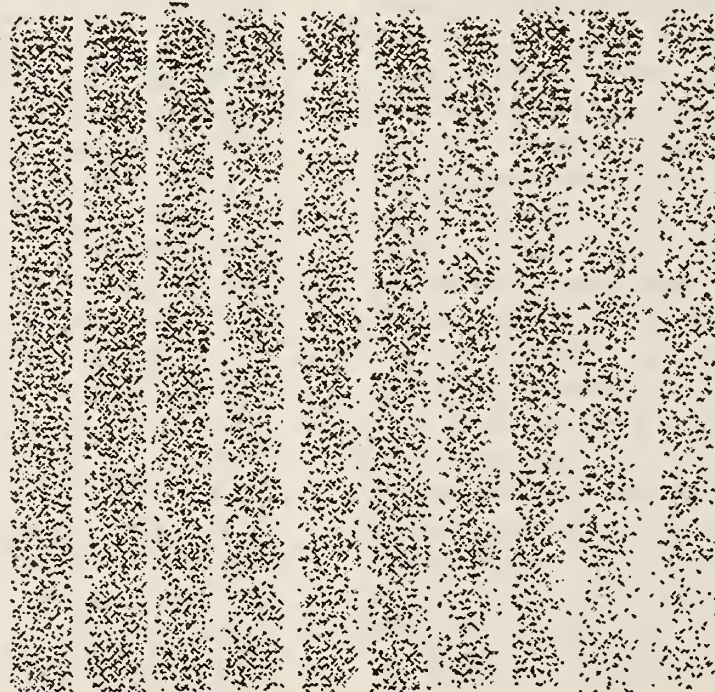


Figure 2. Images of neutron intensities transmitted through polycapillary fibers at various bending radii.

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**CORRECTING TIME-OF-FLIGHT NEUTRON DIFFRACTION DATA  
FOR CHOPPED DELAYED NEUTRON BACKGROUNDS**

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Neutron choppers in pulsed neutron source beams serve to reduce the background caused by delayed neutrons in pulsed source instruments. We have analyzed the effect of a drum chopper placed in an incident pulsed beam which contains delayed neutrons and computed its influence on the detector counting rate. Expressions [1] are found for the time and wavelength dependence of the counting rates for both prompt and delayed neutrons in both the monitor and the scattered neutron detectors.

The transmission probability of a drum chopper has been derived as a function of the time, the neutron wavelength and the geometric parameters [2]. Three separate cases have been found depending on the chopper slot width relative to the incident neutron beam width. In addition, each of these cases depends on the neutron wavelength, the frequency of rotation of the chopper and the diameter of the chopper. The development of these expressions is in the black chopper, first order, parallel beam approximation. These expressions have been used to calculate the open time functions of the drum choppers operated in time-of-flight diffractometers for the suppression of delayed

neutron backgrounds. They can also be used for the calculation of the prompt and delayed neutron counting rates in pulsed source diffractometers.

An exact method is suggested for determining the delayed neutron counting rate, using the prompt and delayed neutrons with the chopper operating in random phase with respect to the source. In addition, we have examined three approximate methods by which the delayed neutron response might be determined in terms of the prompt response; these appeal to the calculated pulse shape functions and might be refined iteratively. These approximate methods serve as a check on the exact random phase chopper method. Measurements have also been taken which confirm the analysis of this random-phase chopper method.

**References**

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**NEUTRON REFLECTIVITY FIT PROGRAMS**

J. F. Ankner

We report here the latest results of our ongoing development of data modeling software for the analysis of neutron specular reflectivity experiments. In addition to programs for non-linear least squares refinement of block profiles using the Nevot-Croce formalism (REFFIT) and discrete micro-layers (BLOCKS), we have during the past year implemented programs for multilayer systems (MLAYER) and exotic interfacial profiles (TAILS) [1].

Layered structures are of both fundamental and practical interest. The program MLAYER simulates the specular reflectivity of multilayer materials and performs least-squares fits to measured profiles. Figure 1 shows the specular reflectivity of 10 bilayers of NiC/TiMn sputtered onto a float glass substrate. This particular multilayer structure is a prototype material for the construction of neutron supermirror guides because of the large contrast between the NiC and TiMn layers. At bulk densities and

concentrations,  $Q_{\text{cNiC}}^2 \approx 7 \times 10^{-4} \text{ \AA}^{-2}$  and  $Q_{\text{cTiMn}}^2 \approx -1 \times 10^{-4} \text{ \AA}^{-2}$ . As can be seen from the inset to figure 1, the scattering densities of the individual layers do not approach these values—indeed, the TiMn layers exhibit a net *positive* density. This behavior indicates that the sample possesses a great deal of interdiffusion between its constituent layers. Reduction or elimination of this interdiffusion is a key step in the development of these films for use as neutron guide materials.

The study of polymer films continues to be a major subfield of materials science. Over the past several years, an important question has been how a polymer, attached at one end to a fixed surface, uncoils into a solvent. Figure 2 shows the reflectivity (closed circles) of such a "polymer brush," consisting of a deuterated polystyrene chain with a carboxyl group at one end attached to a silicon substrate, trailing off into a protonated solvent (cyclohexane,  $\text{C}_6\text{H}_{12}$ ) [2]. We have used the program TAILS and fitted the data to a parabolic density profile 155 Å thick with an 11 Å depletion layer at the interface with the native silicon oxide layer. The inset to figure 2 shows the volume fraction of the polymer in the solution as a function of depth for the profile used to generate the fitted curve. This model fits the data better than either a parabolic profile without a depletion layer, a rectangular profile (fitted using the BLOCKS program), or a power-law tail, and is consistent with theoretical predictions for a polymer brush in a good solvent. The radius of gyration of the polystyrene is 35 Å, meaning that the polymer is stretched to about twice its free-floating length in this system.

We have briefly described two examples of the type of modeling that can now be done using the MLAYER and TAILS programs. Currently, we are working on magnetic multilayers, diblock copolymer films and multilayers, iron oxidation in an electrolytic cell, and protein function in biological membranes. Future improvements to the software include the incorporation of independent magnetic density profiles, modeling the spin-flip specular scattering of nonferromagnetic layers, different functional forms for polymer and magnetic tails, and interfacial profiles other than the standard error function and hyperbolic tangent shapes.

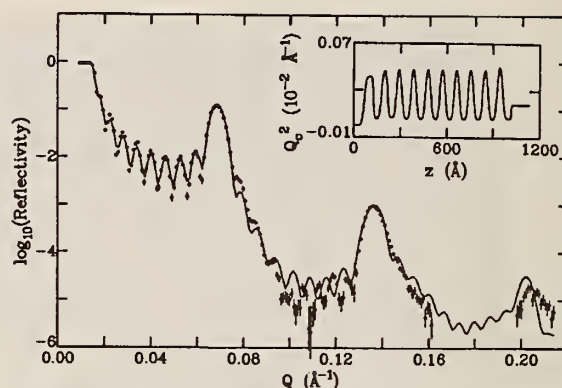


Figure 1. Fit to NiC/TiMn multilayer using MLAYER program. The inset shows the scattering density profile used to generate the solid line.

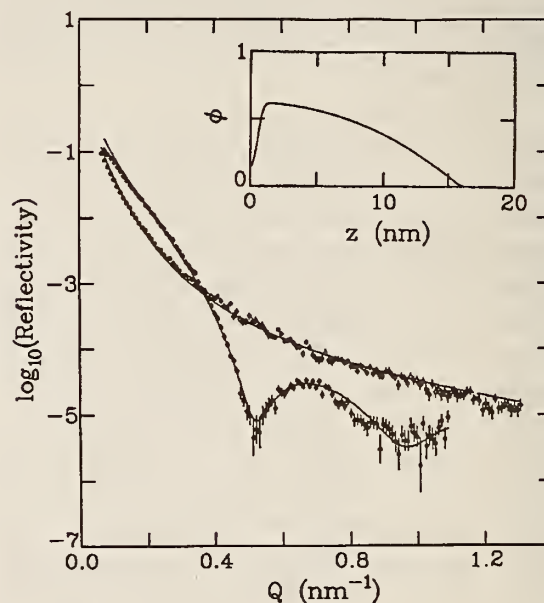


Figure 2. Fit to deuterated polystyrene polymer tail in protonated cyclohexane solvent. The open circles show the reflectivity of the solvent without the polymer, while the closed circles show the same in the presence of polystyrene. The inset shows the volume fraction of the polymer in the solution as a function of depth for the density profile that was used to generate the solid line.

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## PROFILE REFINEMENT IN GRAZING ANGLE DIFFRACTION

J. F. Ankner

The excitation of a diffracted beam under conditions of total external reflection is known as grazing-angle diffraction. The incident beam strikes the sample at an angle below the critical angle for total external reflection, thereby confining the intensity to an exponentially damped layer at the surface, while the sample is oriented such that the in-plane components of the incident and exit wavevectors satisfy a Bragg condition (fig. 1(b)). By means of this geometry, one can use x-rays and neutrons to study in-plane near-surface structures. Grazing-angle diffraction has most often been employed to determine surface structures using the high intensity available at x-ray synchrotron sources. Some experiments have attempted to study structure beneath the surface, but not in a very quantitative fashion. We have developed a formalism whereby one can apply the well-known techniques of specular reflectivity modeling to the determination of depth-resolved in-plane structures in grazing-angle diffraction. Depth-resolved measurements of this kind are especially important for neutron grazing-angle diffraction because of the intrinsically large scattering depths (typically 50-100 Å) of neutrons in matter.

The specular reflectivity of neutrons or x-rays from a refractive boundary is described by the 1-d wave equation. A neutron plane wave  $\vec{k}_0$  incident onto the surface of a material

will excite both reflected and refracted beams within that material. One can describe an arbitrary refractive-index gradient by means of a discrete sequence of steps of constant refractive index. At the interface between two different media, the neutron wave function is (see figure 1(a))

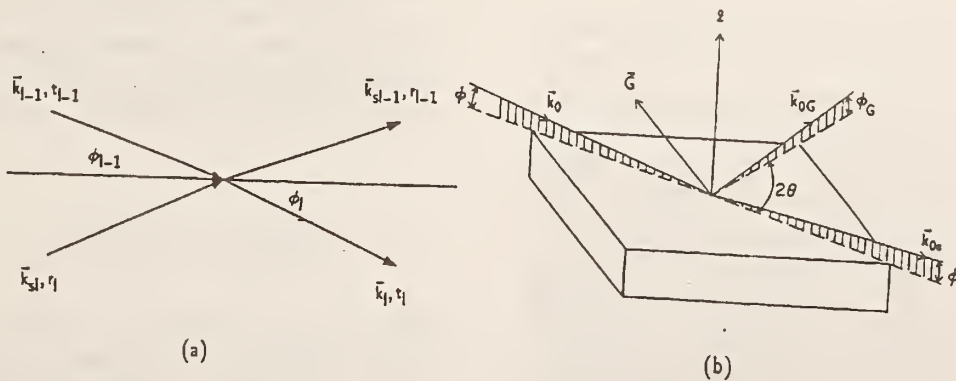
$$\Psi(\vec{r}) = \begin{cases} t_{l-1} e^{i\vec{k}_{l-1} \cdot \vec{r}} + r_{l-1} e^{i\vec{k}_{l-1} \cdot \vec{r}} & (l-1)^{\text{st}} \text{ layer} \\ t_l e^{i\vec{k}_l \cdot \vec{r}} + r_l e^{i\vec{k}_{sl} \cdot \vec{r}} & l^{\text{th}} \text{ layer} \end{cases} \quad (1)$$

where  $\vec{k}_l$  and  $\vec{k}_{sl}$  are the transmitted and specularly reflected wavevectors in refracting layer  $l$  and  $t_l$  and  $r_l$  their amplitudes. According to Snell's Law, only the wavevector components normal to the surface change in specular scattering,

$$\vec{k}_l = \vec{k}_{l0} + \vec{k}_{\perp l} = \vec{k}_{l0} +$$

$$\left( \sqrt{k_{l0}^2 - 4\pi N_l b_l} \right) \hat{n}_{\perp}, \quad (2)$$

where  $N_l$  is the number density of scatterers and  $b_l$  their nuclear scattering length, in general a complex quantity. The subscripts refer to wavevector components parallel and perpendicular to the sample surface. One obtains the



**Figure 1.** (a) A beam incident on the interface ( $\vec{k}_{l-1}, t_{l-1}$ ) excites reflected ( $\vec{k}_{sl}, r_{l-1}$ ) and refracted ( $\vec{k}_l, t_l$ ) waves, with a beam reflected from the next lowest interface ( $\vec{k}_{sl}, r_l$ ) also possibly being present. (b) In grazing-angle diffraction, the sample is aligned such that a diffracted beam ( $\vec{k}_{0G}$ ) is excited simultaneously with the specularly reflected beam.

amplitudes  $t_l$  and  $r_l$  by applying as boundary conditions the continuity of  $\Psi$  and  $\hat{\nabla} \Psi \cdot \mathbf{n}_\perp$  and recalling that  $\mathbf{k}_{s1} = \mathbf{k}_1 - 2(\mathbf{k}_1 \cdot \hat{\mathbf{n}}_\perp)\hat{\mathbf{n}}_\perp$ ,

$$t_{l-1}e^{ik_{\perp l-1}d_{l-1}/2} + r_{l-1}e^{-ik_{\perp l-1}d_{l-1}/2} = t_l e^{-ik_{\perp l}d_l/2} + r_l e^{ik_{\perp l}d_l/2}, \quad (3)$$

$$(t_{l-1}e^{ik_{\perp l-1}d_{l-1}/2} - r_{l-1}e^{-ik_{\perp l-1}d_{l-1}/2})k_{\perp l-1} = (t_l e^{-ik_{\perp l}d_l/2} - r_l e^{ik_{\perp l}d_l/2})k_{\perp l}, \quad (4)$$

where  $d_l$  is the thickness of refracting layer  $l$ . Solving the above equations for the ratios  $r_{l-1}/t_{l-1}$  and  $r_l/t_l$  one obtains the well-known Parratt recursion formula [1],

$$R_{l-1} = a_{l-1}^4 \left[ \frac{R_l + F_{l-1,l}}{R_l F_{l-1,l} + 1} \right], \quad (5)$$

where

$$R_l = a_l^2 \frac{r_l}{t_l}, \quad (6)$$

$$a_l = e^{ik_{\perp l}d_l/2}, \quad (7)$$

and

$$F_{l-1,l} = \frac{k_{\perp l-1} - k_{\perp l}}{k_{\perp l-1} + k_{\perp l}}. \quad (8)$$

This recursion relation forms the basis of the modeling schemes commonly employed in reflectivity analysis, where one measures the specularly reflected intensity  $|r_0|^2$ .

Grazing-angle diffraction from ideally imperfect crystals can be described by the distorted wave approximation, which splits the scattering problem into two parts: a kinematical solution of the in-plane Bragg diffraction and a dynamical treatment of the specular reflectivity. One can modify the conventional treatment of grazing-angle diffraction from a monolithic slab to study the effect of buried layers of different

composition and/or structure on the diffracted intensity [2,3],

$$I(\vec{Q}) = I_0 \left| \sum_l F_l(\vec{Q}_\parallel) \delta(\vec{Q}_\parallel - \vec{G}_l) * t_l(k_{\perp 0}) \frac{e^{iQ_l M_l d_l} - 1}{e^{iQ_l d_l} - 1} t_l(k_{\perp 0} G) \right|^2, \quad (9)$$

the  $l$  summation runs over the buried slabs with structure factors  $F_l$ , reciprocal lattice vectors  $\vec{G}_l$  containing  $M_l$  layers of thickness  $d_l$  with  $\vec{Q} = \vec{k}_{G_l} - \vec{k}_1$ . The illuminating amplitudes and all of the phase information about the specular process are included in the transmittivity factors, which are given by equations (3)-(8),

$$t_l = \frac{a_l}{a_{l-1}^3} \left( \frac{a_{l-1}^4 - F_{l-1,l} R_{l-1}}{1 - F_{l-1,l}} \right) t_{l-1}. \quad (10)$$

This relationship suggests that any measurement of depth-resolved grazing-angle diffraction must begin with a thorough specular reflectivity characterization in order to obtain the  $t_l$  as fixed parameters. One could then study, for example, surface-induced ordering, strain profiles, or magnetization variation with depth, as well as multilayer effects.

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# RESOLUTION CONSIDERATIONS FOR POLARIZED TRIPLE-AXIS SPECTROMETRY

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and

R. W. Erwin

The polarized beam triple-axis technique is known to be a very powerful method for identifying the origin of both magnetic and nuclear cross sections [1]. For example, with the incident neutron polarization  $\hat{P}$  parallel to the momentum transfer  $Q$ ,  $\hat{P} \parallel Q$ , ferromagnetic spin waves can only be observed for spin-flip scattering, and in fact for the  $(-+)$  configuration the spin waves can only be observed for neutron energy loss scattering, while for the  $(+-)$  configuration spin waves can only be observed in neutron energy gain. For  $\hat{P} \perp Q$ , on the other hand, the  $(+-)$  and  $(-+)$  cross sections are equal in strength for energy gain and energy loss, and one-quarter the intensity of the  $\hat{P} \parallel Q$  situation. Such selection rules are often utilized to separate and identify cross sections. However, when the relative orientation of  $\hat{P}$  and  $Q$  varies substantially over the extent of the instrumental resolution function, substantial distortions of the expected scattering intensities can occur, in addition to the usual resolution effects applicable to unpolarized neutron scattering. The corrections are largest in cases when the resolution is very coarse, as would be expected. The resolution effects are also large when measurements are made at small wave vectors, as is necessary for amorphous materials, and this is the case of particular interest here.

The angular dependence of the polarized neutron cross section for spin wave creation (minus sign) and destruction (plus sign) is given by [2]

$$\frac{d^2\sigma}{d\Omega^2} \propto 1 + (\hat{Q} \cdot \hat{M})^2 \mp 2 (\hat{P} \cdot \hat{Q})(\hat{Q} \cdot \hat{M}) \quad (1)$$

where  $\hat{Q}$  and  $\hat{M}$  are unit vectors in the directions of  $Q$  and the magnetization  $M$ . In the horizontal field configuration  $\hat{Q} \cdot \hat{M} = 1$  and  $\hat{P} \cdot \hat{Q} = \pm 1$ , and equation 1 reduces to  $2 \pm 2P$ , so that for spin wave creation we have the maximum value

of 4 with  $P = -1$   $[(-+)$  configuration] and 0 for  $P = +1$   $[(+ -)$  configuration]. For spin wave destruction we have 4 for  $P = +1$   $[(+ -)]$  and 0 for  $P = -1$   $[(-+)]$ . On the other hand for the vertical field configuration we have  $\hat{Q} \cdot \hat{M} = 0$  and  $\hat{P} \cdot \hat{Q} = 0$ , and the cross section for energy gain and energy loss is unity and independent of  $\hat{P}$ . Hence for either the  $(-+)$  or  $(+-)$  configuration we will see equal intensities of spin waves in energy gain and energy loss.

If the instrumental resolution allows the direction of  $Q$  to deviate substantially from  $M$ , then we must take this angular variation into account when convoluting the resolution with the appropriate cross section. In the horizontal configuration  $\hat{Q} \cdot \hat{M} = \cos\theta$ , and equation 1 becomes

$$\frac{d^2\sigma}{d\Omega^2} \propto 1 + (1 \mp 2P)\cos^2\theta \quad (10)$$

so that we obtain  $1 + 3\cos^2\theta$  for  $(-+)$  and  $(+-)$  in energy loss and energy gain, respectively, and  $1 - \cos^2\theta$  for  $(+-)$  and  $(-+)$  in loss and gain. In the vertical field configuration we have

$$\frac{d^2\sigma}{d\Omega^2} \propto 1 + (1 \mp 2P)\sin^2\phi \quad (11)$$

where we have defined  $\phi = \pi/2 + \theta$ . Then we obtain  $1 + 3\sin^2\phi$  for  $(-+)$  and  $(+-)$  in energy loss and energy gain, respectively, and  $1 - \sin^2\phi$  for  $(+-)$  and  $(-+)$  in loss and gain.

These angular variations are important for the case of amorphous systems, in which the spin waves are only well defined around near  $Q = 0$  and the typical coarse vertical resolution therefore can be a substantial fraction of  $Q$ . To illustrate the nature of the effects we chose the particular case of a ferromagnet with dispersion

relation  $E_{sw} = Dq^2$ . Typical experimental parameters for these types of measurements are  $E_i = 14.8$  meV, and collimation (FWHM) of  $10'-10'-10'-20'$ . We took a convenient value of  $D = 70$  meV-Å<sup>2</sup>. The kinematical details of these types of scans are given elsewhere [3].

Figure 1 shows the convolution of the polarized spin wave cross sections with the instrumental resolution function [4] for the vertical field situation,  $\hat{P} \perp \mathbf{Q}$ , and  $(-+)$  spin-flip scattering. The vertical resolution in this case was chosen to be  $0.1$  Å<sup>-1</sup>. For  $q = 0.05$  Å<sup>-1</sup> the ratio of the energy loss ( $E > 0$ ) to energy gain ( $E < 0$ ) peak is 2.1, while the ideal case where  $\hat{P} \cdot \mathbf{Q} = 0$  this ratio is 0.9, and is given by the  $k_f^3 \cot \theta_A$  resolution factor for the analyzer [4] (and a very small contribution from the detailed balance factor). With increasing  $q$  the ratio becomes closer to the ideal, and for  $q = 0.1$  Å<sup>-1</sup> the ratio has decreased to 1.2.

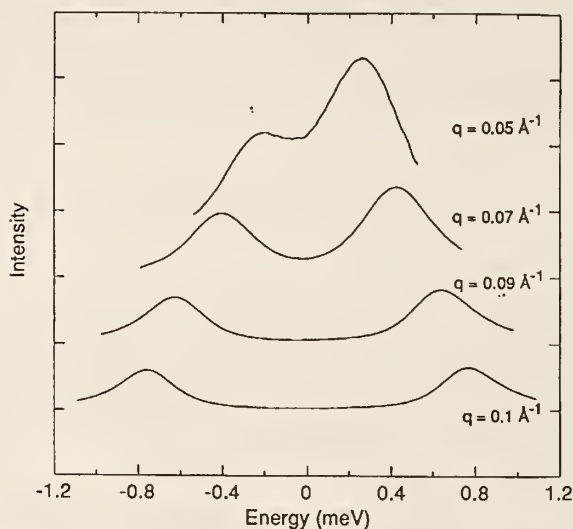


Figure 1. Spin-flip (spin wave) scattering as a function of  $q$ . The ideal ratio of energy loss to energy gain is  $\sim 0.9$ , while the effect of the vertical resolution ( $Q_z = 0.1$  Å<sup>-1</sup>) is to make this ratio greater than unity. The instrumental distortion of the intensity of the peaks is seen to decrease with increasing  $q$ , as the effect of the vertical resolution becomes less important.

The effect of the vertical resolution is shown in figure 2, where the ratio of the energy loss to energy gain peak at  $q = 0.1$  Å<sup>-1</sup> is plotted as a function of the vertical component of the resolution. For tight vertical resolution we get the ideal ratio given by  $k_f^3 \cot \theta_A$ , and then this ratio rapidly increases with increasing  $Q_z$ . These calculations are in 'semi-quantitative' agreement with our recent measurements on the amorphous Fe<sub>86</sub>B<sub>14</sub> system [5], while for complete agreement we must include the energy-dependent reflectivity of the analyzer crystal, which has not been accurately measured yet.

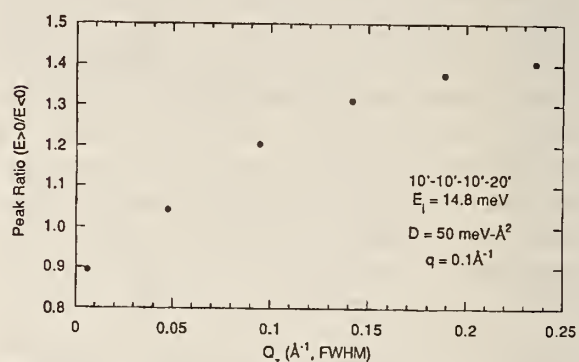


Figure 2. Ratio of the energy loss to energy gain intensities as a function of the component of vertical resolution. The ideal ratio is 0.89, given by the  $k_f^3 \cot \theta_A$  factor.

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## SCATTERING EFFECTS IN SPHERES

J. R. D. Copley and J. M. Rowe

In a neutron beam experiment the rate of any given absorption can be significantly modified depending on the overall absorption cross section of the sample, the nature and magnitude of its scattering cross section, and its shape and size. This phenomenon has recently been investigated analytically [1], using an adaptation of Sears' [2] formalism for the treatment of slow neutron multiple scattering. In our previous work we also described Monte Carlo calculations for slab samples of various shapes and sizes, always assuming the scattering was both elastic and isotropic [1].

Following a suggestion of Fleming [3], we have now extended our calculations to the special case of spherical samples [4]. We have made calculations for pure absorbers, pure scatterers, and samples which both absorb and scatter neutrons. The calculated quantity is either  $[\phi(r)/\phi_0]$ , which is the average flux at points distant  $r$  from the center of the sphere, relative to the external flux  $\phi_0$ , or else the "self-shielding factor"  $f$ , which is the volume-averaged value of  $[\phi(r)/\phi_0]$ :

$$f = \frac{1}{V\phi_0} \int_0^R 4\pi r^2 \phi(r) dr,$$

where  $V$  is the volume of the sphere and  $R$  is its radius.

We have compared the Monte Carlo calculations with independent numerical calculations using an iterative technique to solve the neutron transport equation. The Monte Carlo calculations assumed a monodirectional incident beam of neutrons whereas the iterative calculations were performed for a sphere in an isotropic field, and in every comparison the agreement was very satisfactory. This strongly suggests that the calculations are correct, and that the calculated quantities, defined above, are independent of the directional nature of the neutron field. This last result is intuitively appealing and has been rigorously derived [4]. We have also succeeded in proving and demonstrating that  $f = 1$  for a purely scattering

sphere, or indeed for a purely scattering sample of arbitrary shape placed in an isotropic field of neutrons [4].

In figures 1 and 2 we show results from our Monte Carlo calculations for spheres which both scatter and absorb neutrons. Figure 1 shows the flux ratio  $[\phi(r)/\phi_0]$  as a function of  $(r/R)$  for several choices of  $x_A = 2\Sigma_A R$  and  $x_S = 2\Sigma_S R$ , where  $\Sigma_A$  and  $\Sigma_S$  are respectively the macroscopic absorption and scattering cross sections within the sphere. The good agreement between Monte Carlo and iterative numerical calculations is apparent. Also shown are the results of diffusion theory calculations which work well except at points close to the surface of the sphere and when  $\Sigma_A$  is large.

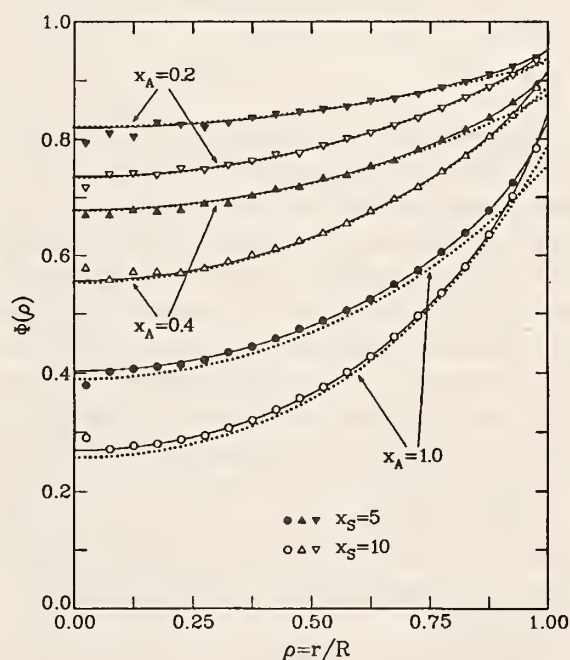


Figure 1. Flux distributions within spheres, calculated by Monte Carlo (points) and by an iterative numerical technique (solid lines). Results obtained using diffusion theory are shown as dotted lines. The ordinate is identical to  $[\phi(r)/\phi_0]$ .

Figure 2 shows the dependence of the self-shielding factor  $f$  on  $x_A$  and  $x_S$ . An increase in the scattering cross section clearly decreases  $f$  if  $\Sigma_A$  is held constant, but an important conclusion

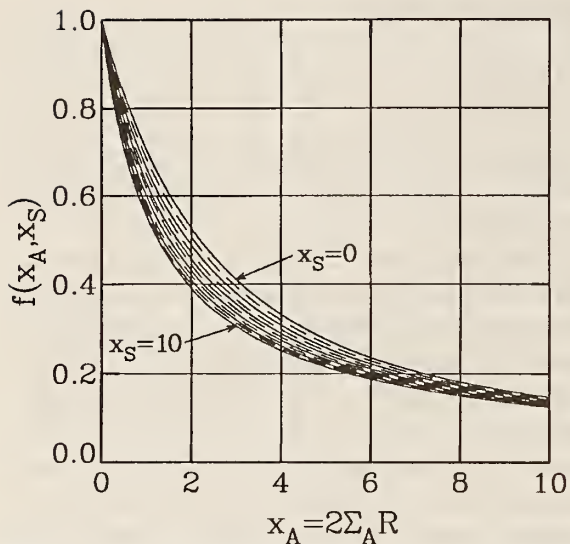


Figure 2. The self-shielding factor  $f(x_A, x_S)$ , plotted as a function of  $x_A$ , for integer values of  $x_S$  between 0 and 10.

is that  $f$  is less sensitive to  $\Sigma_S$  than in other commonly chosen sample geometries. This conclusion is consistent with the experimental prompt gamma neutron activation analysis results reported by Mackey and coworkers [5].

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## REACTOR OPERATIONS AND ENGINEERING

T. M. Raby, J. H. Nicklas, and J. F. Torrence

Reactor operation during the past year has been uneventful and essentially routine. The reactor operated approximately 90% of all available reactor time. The small amount of lost time was mainly caused by minor heat exchanger leaks and outside electrical power interruptions. Fuel utilization continues to be the best in the United States and will improve further in the coming years. Reactor utilization is at its peak. Highlights of significant items are outlined below.

**Guide Tubes.** The first three cold neutron guide tubes became fully operational. The isolation valve for a fourth tube was installed and successfully tested clearing the way for installation of the guides.

**Main Heat Exchangers.** Minor leaks continued to develop in one of the main primary heat exchangers. The size of the leak was so small, on the order of one drop a minute, that it was virtually impossible to find among the 1200 tubes of the exchanger. This has caused extra days of shutdown plus added exposure to personnel. In April 1991, the leaky heat exchanger was removed from service. Operations continued utilizing the remaining heat exchanger at reduced power. Analysis indicated that a

maximum of 15 MW of power could be achieved under almost all weather conditions. This turned out to be not only the maximum but the optimum for operation with a single heat exchanger. Operations in this mode will continue for the foreseeable future. The leaky heat exchanger is being monitored and maintained and could be returned to service if needed. Negotiations for new replacement heat exchangers of a different plate-type design have been completed. Special emphasis on quality and reliability have been incorporated in the specifications. Fabrication is scheduled to begin in late summer of 1991.

**New Advanced Fuel.** The fifth generation of advanced fuel elements was introduced into the reactor in April 1991. This will further improve fuel utilization thereby extending the operating cycle. The new elements are the heaviest loaded in the history of the facility and contain more than twice the uranium loading of the original elements. This loading is the highest that can be used at the NBSR.

**Control Room Upgrade.** Plans are being prepared for a complete upgrade of the reactor control room once funding becomes available.

## FACILITIES, OPERATIONS, AND TECHNIQUE DEVELOPMENT

Meantime, several segments and components have been modernized and upgraded.

Staffing. Two new operators received NRC senior licenses with high marks. The staff of 16 operators, the smallest for any comparable reactor,

all hold senior licenses. Two senior nuclear engineers are spending a one-year sabbatical at the Division and will be assisting in the reactor modernization plan.

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## PRACTICAL APPLICATIONS OF NUCLEAR RESEARCH REACTORS

B. Hammouda

Most people associate nuclear energy with weapons programs and electrical power production. While it is true that these two applications are the most important ones, there is a host of other very beneficial applications of nuclear energy that are not as well known. Some of these are described in a report put together by this author for a series of lectures. These include: neutron activation analysis, radioisotopes applications, neutron radiography, neutron gauging, neutron depth profiling, radiation effects and applied neutron scattering.

Neutron activation is an analytical technique used to detect and quantify minor and trace levels of elements for a wide variety of applications encompassing many fields of physical, natural, and life sciences. It allows a precise "fingerprinting" of objects based on their radioactive decay following neutron activation. This technique has found various biomedical, geological, archeological, forensic science, art history, industrial, and environmental applications. It is used, for example, to trace ancient artifacts to their place of origin therefore allowing archeologists to infer routes of trade and population migrations. It is also routinely used by some law enforcement authorities to detect traces of gunshot on the hands of crime suspects.

The need to use radioisotopes has been growing ever since their discovery, i.e., since the advent of particle accelerators and nuclear reactors. Radioisotopes produced using nuclear reactors are beta and/or gamma emitters and can be produced in substantial quantities. They found wide spread applications in medical, industrial, agricultural, and environmental fields. Cobalt-60 applications, for example, are well

known for their wide use in radiation therapy, for the "radurization" of foods and for the sterilization of medical supplies. Another example is the attachment of Mo-99 to monoclonal antibodies to seek and destroy cancer cells through beta emission.

Three kinds of applications (neutron radiography, neutron gauging and neutron depth profiling) are sometimes referred to as "neutron interrogation". Neutron radiography is another very much unknown application (compared to X-ray radiography, for example). Yet, this technique is very useful for visualizing contrasts between various elements as well as in following real time dynamics of hydrogen-containing fluids. Neutron gauging is used in mining operations to produce indirect imaging of geological layers, in industrial bulk process streams for the grading of ores, and in commercial applications to determine the hydrogen and nitrogen contents of various food stuffs (nuts, grains, etc). Neutron depth profiling is a recently-developed technique for the characterization of the density profile of some prompt charged particle emitters (boron for example) following neutron absorption close to a sample's surface.

The radiations produced in reactors (fast neutrons, gamma rays) have strong "effects" on materials. Note that the word "damage" is sometime used in this context with a negative connotation, whereas these effects can be useful such as in track etching (a form of dating over a range of ten billion years), in the transmutation doping of silicon to produce semiconductors, in the coloration of gemstones through the introduction of color centers, and through radiation hardening of various hard working

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mechanical components (drill bits for example). Microporosity produced by fission tracks in uranium doped glass is essential in High Performance Liquid Chromatography. Track etching is also used to produce the best plastic filters available for chemical and pharmaceutical applications. Also, fast neutron irradiation of memory units in bulk can reduce the probability of occurrence of random bit resets in computers.

The field of neutron scattering uses thermal or cold neutrons as a diagnostic probe to investigate the structure, phase transitions and dynamics of a wide variety of materials. There are some very practical aspects of neutron

scattering such as in the monitoring of microstresses in engineering materials, the estimation of porosity in coals, etc.

Most of the practical applications of nuclear research reactors have started as limited research projects. Some of them have matured enough that they have become viable business ventures operated as a "service" to earn much needed funds in the national laboratory and university based reactors. However, as yet, no research reactor has been built by an industrial firm for profit making only, through the exploitation of such applications.

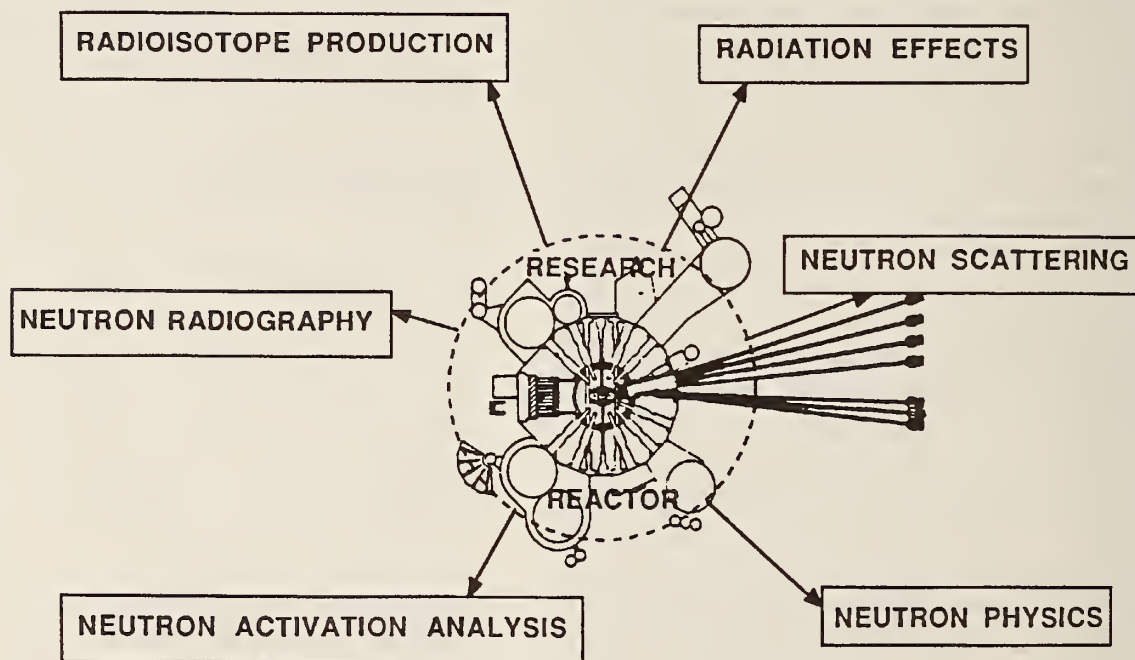


Figure 1. Practical applications of nuclear research reactors.

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# ACTIVATION DETERMINATION FOR NBSR IRRADIATED FUEL ELEMENT HARDWARE (NONFUEL SECTIONS) AND SPENT SHIM ARMS ASSEMBLIES

D. R. Brown (Reactor Health Physics)

In November 1990 a waste shipment containing irradiated fuel element hardware (non-fuel sections) and spent shim arm assemblies was packaged and shipped to Barnwell, SC, for processing and burial. Regulations required specific nuclide activity determinations for the entire shipment. The resulting project involved confirmation of elemental composition of materials used for element and shim arm fabrication, neutron activation measurements and calculations, regional core and vessel neutron flux imaging as well as direct dose rate measurements.

**Material Composition.** Elemental composition of fabrication materials was determined via several methods and comparisons. Initially, data from ASTM standards and material batch certification of micro-alloying constituents and residual trace contaminants, were used to estimate activity. This, however, did not support results from direct measurements. Samples of material were machined from a clean, disassembled fuel element head piece for neutron activation analysis. Major elements in this analysis were in good agreement with published standards.

## Activity Calculations and Measurements.

Direct measurements were made of each non-fuel section (4) of a selected element with a known core history. Measurements were made using a portable germanium detector and multichannel analyzer set up at a considerable distance. The predominate nuclides in this measurement were  $^{60}\text{Co}$  and  $^{65}\text{Zn}$ . Activity was determined using free air gamma dose rate measurements and tabulated  $I_\gamma$  dose rate conversion factors for  $^{60}\text{Co}$  and  $^{65}\text{Zn}$ .

These computed activities were then used to ascertain the average neutron fluence for each element region/section. Using fuel element histories and assuming a 'flat' neutron flux distribution, radially across the core, fluence was calculated from measured activity and known nuclear properties of materials irradiated. The results correlated well with data available in NBSR-9 and flux mapping data available from irradiation facility (rabbit tubes and verticle thimble(G2)) experimental measurements. The neutron fluences were then used to calculate the remaining unmeasurable activation products.

MATERIAL COMPOSITION AND ACTIVATION DATA

	6061 Aluminum			30X Stainless Steel*			Cadmium	
Elemental Composition	Al-99%+	Cu-.36%	Fe-.33%	Fe- 84%	Cr- 22%	Ni- 11%	Natural Cd Metal	
	Cr-.09%	Zn-.06%	Ti-.03%	Co-.22%	Mo-.22%	Sb-.003%		
	Co-.0003%	Hf-.0002%						
Activation Products	$^{60}\text{Co}$	$^{65}\text{Zn}$	$^{59}\text{Fe}$	$^{60}\text{Co}$	$^{51}\text{Cr}$	$^{59}\text{Ni}$	$^{109}\text{Cd}$	$^{109\text{m}}\text{Ag}$
	$^{46}\text{Sc}$	$^{181}\text{Hf}$	$^{55}\text{Fe}$	$^{63}\text{Ni}$	$^{58}\text{Co}$	$^{99}\text{Tc}$	$^{113\text{m}}\text{Cd}$	$^{110\text{m}}\text{Ag}$
	$^{185}\text{Hf}$	$^{45}\text{Ca}$	$^{51}\text{Cr}$	$^{124}\text{Sb}$	$^{59}\text{Fe}$	$^{55}\text{Fe}$	$^{115\text{m}}\text{Cd}$	$^{110}\text{Ag}$

\* - CONSTITUENTS ADD UP TO >100% DUE TO APPROXIMATIONS IN CALCULATIONS.

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## Reference Element - #NBS-492

Date in Core - 10/6/88 Date to Pool - 2/18/88

Date last irradiated - 2/2/88 MWHrs 101,896 (7 cycles)

Table 1. Fuel element section dose rate measurements and activity calculations - 2/7/90

Section	Dose Rate @ 8.5 m mR/hr	Dose Rate @ 14.2 m * mR/hr	Nuclide	Activity μCi
Head	8.0	2.7	<sup>60</sup> Co	337
			<sup>65</sup> Zn	7
Long Box	1.6	0.6	<sup>60</sup> Co	44
			<sup>65</sup> Zn	91
Mid-Fuel	1.6	0.6	<sup>60</sup> Co	51
			<sup>65</sup> Zn	112
Bottom	1.3	0.6	<sup>60</sup> Co	40
			<sup>65</sup> Zn	70

\* - ALSO DISTANCE FOR GAMMA SPEC MEASUREMENT

Table 2. Reference fuel element activity  
---decay corrected to 11/15/90---

Nuclide	½-life	Activity 2mCi
<sup>60</sup> Co	5.27 Y	445.9
<sup>65</sup> Zn	244 D	124.8
<sup>59</sup> Fe	44.5 D	5.7E-5
<sup>55</sup> Fe	2.74 Y1	351.7
<sup>59</sup> Ni	7.5E4 Y	0.1
<sup>63</sup> Ni	100 Y	16.9
<sup>51</sup> Cr	25 D	3.1E-7
<sup>58</sup> Co	71 D	2.8E-3
<sup>124</sup> Sb	60 D	1.4E-5
<sup>46</sup> Sc	84 D	5.9E-5
<sup>181</sup> Hf	42 D	3.9E-6
<sup>185</sup> Hf	70 D	3.9E-4
<sup>99</sup> Tc	2.13E5 Y	1.2E-7
Total Activity ≈ 1940 mCi		

This same procedure was followed for the shim arms with some variation. The shim arms do not remain in the same flux region throughout a reactor cycle, hence, corrections must be made. Self shielding is also a factor to be considered when evaluating the shim arms.

Total activity of shipment of 128 unfuelled fuel elements and 4 shim arm assemblies was approximately 400 curies, as of the ship date in November 1990. The dominate nuclide in terms of total activity was <sup>55</sup>Fe.

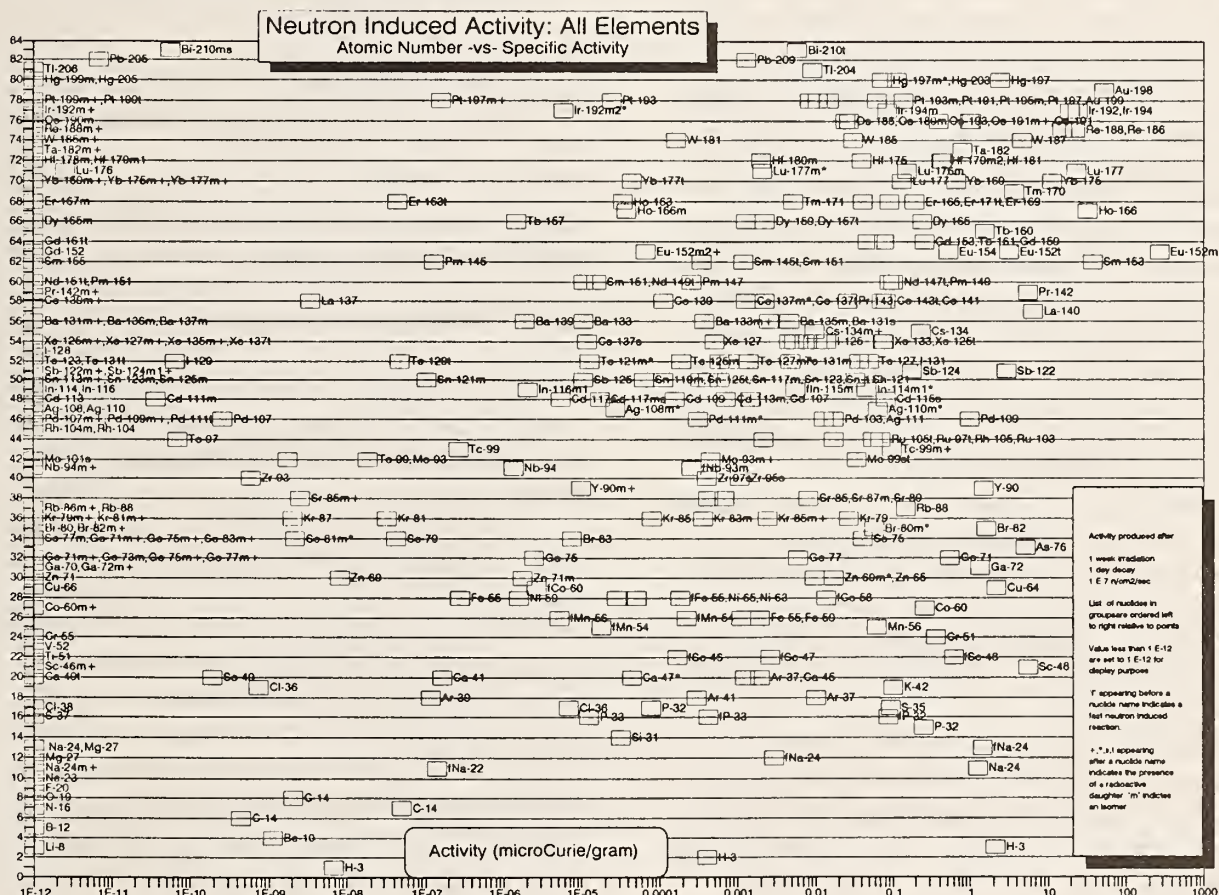
# FACILITIES, OPERATIONS, AND TECHNIQUE DEVELOPMENT

## NEUTRON ACTIVATION DATABASE

L. A. Slaback (Occupational Health and Safety Division)

A personal computer based database in a spreadsheet format was prepared for the evaluation of the activation characteristics of experimental samples. Cross-section data from the IAEA [1] was used. The fast neutron reaction data was weighted assuming a fission

spectrum. Provision for production via epithermal reactions and radioactive daughters is included. The figure 1 displays the results of a calculation for all elements for typical irradiation conditions at the NBSR experimental facilities.



Notes related to the figure: Each radioactive nuclide computed by the database is displayed, with the ordinate being the atomic number. The conditions for the calculation are:  $1 \times 10^7$  neutrons  $\text{cm}^{-2} \text{sec}^{-1}$  (fast or thermal), one week irradiation, one day decay (which suppresses the very short lived materials), and one gram of the natural element. The cadmium ratio is taken as zero, e.g., the epithermal cross-section is suppressed. For display purposes results of less than  $10^{-12}$  microcuries per gram are shown as that value. All points are labeled except for several xenon, cadmium, and tellerium nuclides. Where the labels are grouped the left-to-right order of the labels correspond to the unlabeled points on a left to right order. Those reactions produced by fast neutrons are identified by a 'f' in front of the nuclide label. The symbols +, \*, s, t appearing after a nuclide name indicate the presence of a radioactive daughter. The differing indicators relate to different calculational treatments due to the presence of that daughter. Several radioactive daughters that result only from the decay of an induced parent are included in these results, primarily when the daughter is longer lived than the parent.

### Reference

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RESPONSE TESTS FOR A NBSR SECONDARY SYSTEM ON-LINE  $H^3$  MONITOR

T. F. Mengers (Occupational Health and Safety Division)

This report is a summary of the development of a continuous flow liquid scintillation counting system to monitor  $H^3$  concentrations in the NBSR secondary cooling loop.

Before operating our on-line  $H^3$  monitor we tested three different brands of "environmentally safe" cocktails: Berthold Flow-5; Packard Instagel; and Beckman Ready-Safe. The environmentally safe scintillants can be released to the sanitary sewage system if the  $H^3$  concentrations are sufficiently low. These tests were the basis for our choice of scintillant and ratios. We desired high sample to scintillant ratios to increase response (by having more sample in the counting volume) and minimize scintillant consumption. Irregularities were observed in the response curves (cpm/ml of sample vs. ratio) corresponding with inhomogeneous mixing, opacity, or gelling at higher sample-to-scintillant ratios. This indicated a maximum acceptable sample to scintillant ratio of 1:4.

Benchtop tests were used to evaluate total flow rates and minimum response times. We then connected the monitor to the secondary system and began operational tests. Figure 1 indicates the system response to a high  $H^3$  concentration shortly after start-up following a tube leak repair. The dots indicate the secondary  $H^3$  concentrations measured by liquid scintillation analysis of secondary basin grab samples. The graph illustrates some of the failure modes associated with the on line monitor.

The intermittent dips in the count rate are presumed to be due to small air bubbles introduced into the system. The sudden drop is due to plugging of the capillary tube on the sample inlet. Plugging is caused not only by scintillant gelling, but also by fouling due to impure secondary water and corrosion on fittings. The frequency of plugging is greatly reduced if we purge the capillary lines every other day using a 10 ml syringe and the priming valve on the 110B pump. We also perform a periodic "fast flow" purge by fully opening the

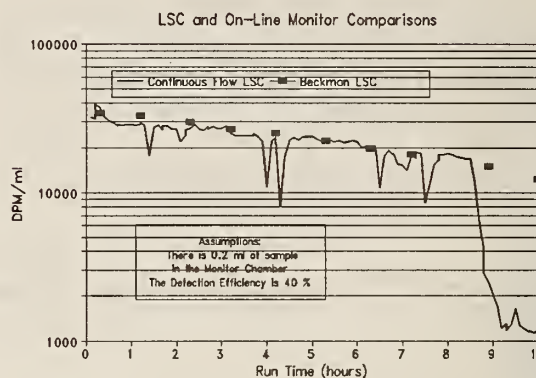


Figure 1. Tritium concentrations in the secondary cooling system after plugging a leak in the heat exchanger.

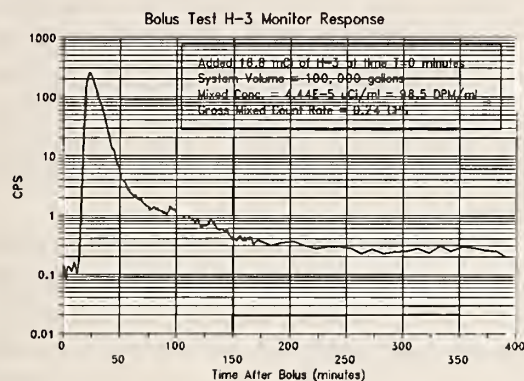
sample throttling valve and running the two pumps at the maximum flow rates. This does not appear to significantly disrupt the sample to scintillant ratios or affect the count rate records. These operations can be performed in less than 10 min.

The balance of scintillant and sample flow rates is critical to system calibration since this determines the amount of sample in the fixed volume of the counting chamber. Set-up factors that influence this balance include: the elevations of the scintillant supply and effluent containers relative to the pumps; and the sample supply line pressure. The scintillant supply must be below the pump inlet. The effluent tank must be above the monitor and pumps to prevent a siphoning action which disrupts the flow rates. Also, the sample supply lines must have a vent and overflow to allow atmospheric pressure on the pump inlet, otherwise the pump allows unmeasured flow-through which disrupts calibration.

Figure 2 illustrates the response of the monitor to a bolus of  $H^3$  introduced into the secondary system at the  $N^{16}$  monitor prefilter. We added  $16.81 \pm 0.85$  mCi (47 ml) to the system.

The rise to a peak began at roughly 12 min. The bolus actually passed the tap off for the  $H^3$  monitor within 2 min and it took an additional 10 min for the sample to be drawn into the

## FACILITIES, OPERATIONS, AND TECHNIQUE DEVELOPMENT



**Figure 2.** Continuous H-3 monitor response after adding a bolus of 16.8 m Ci of  $H^3$  to the secondary system.

counter. Results for a sequence of samples taken at the top of the basin were used to verify estimates of the secondary sample volume. After adjusting for a blow down rate of 110 GPM the calculated secondary system volume averaged to be  $106,094 \pm 5957$  gal (1  $\sigma$ ). This agrees well with estimates of 100,000 gal based on piping dimensions measurements.

The monitor required a substantial amount of time to return to the equilibrium levels which

were obtained by complete mixing at the basin in less than 20 min. Presumably this is due to the slow sampling flow rate and relatively large volume of the throttling valve and vent tubing. There may also be some residual contamination of the sample line tubing. The system exhibited similar clearance delays following benchtop tests before connection to the secondary system.

Our current configuration uses a 1:4 sample to scintillant ratio with a total flow 0.75 ml/min. We attempted initially to run at half that flow rate but we obtained inconsistent results. The current ratio results in 0.2 ml of sample in the counting chamber at all times. We have obtained 56.3 cps for a secondary concentration of  $1.5E-2$  uCi/ml and 0.25 CPS (roughly twice background) for secondary concentrations as low as  $4.4E-5$  uCi/ml. Therefore the overall counting efficiency is approximately 40%.

Our annual scintillant consumption is around 320 liters per year which costs roughly \$3200. This cost is justified by the potential for faster response time for detecting a major heavy water leak.

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## REACTOR BUILDING AREA MONITORING USING THERMOLUMINESCENT DOSIMETERS

T. Mengers (Occupational Health and Safety Division)

Starting in the last quarter of 1989, TLD monitors have been placed in twenty-eight locations throughout and around the facility. The monitoring stations include: eleven locations around the walls of the guide hall; five outside surrounding the guide hall; five in the offices of the A and E wings facing the guide hall; four in the offices along the front of building 235; one by the control room door; one in the pump house; and one in the high bay. The primary goal of this monitoring is to assess the impact of the new guide hall experimental stations on unrestricted area doses.

During the last quarter of 1989 and most of the first quarter of 1990 the reactor was in an extended outage for neutron guide installation.

The TLD data collected during this time serves as a baseline.

Comparisons of the first two graphs in figure 1 (Baseline) with the second two graphs in figure 2 reveals several things. None of the measurements in the unrestricted areas outside the guide hall or in the office wings indicated significant increases due to guide hall operations. The neutron dose equivalents at some the monitors (BR2, BR3, and BR4) on the guide hall wall increase by a factor between two to eight, but this remains a minimal part of the total dose equivalent. These increases are related with the proximity to and use of the prompt gamma facility on NG7. Changes in the experiment shielding have reduces or removed even these small doses. The gamma dose rates at these

## FACILITIES, OPERATIONS, AND TECHNIQUE DEVELOPMENT

locations increased by as much as a factor of four.

Elevated dose rates at around BR8 are due to radwaste shipment work in or near the guide hall truck bay. The maximum daily averaged dose equivalent measured was 1.01 mrem/day. This dose rate is less than 20 % of the regulatory limits for areas outside the building.

In addition to the measurements made around the guide hall, four offices along the front of building 235 were monitored as control points. The maximum dose equivalent rate (gamma plus neutron) was 0.166 mRem/day and does not indicate any correlation with reactor operations. These locations do display a slightly increasing trend in neutron dose equivalents with respect to the proximity to building 245. This trend was also seen in the TLDs located outside

the guide hall. The trend was indicated consistently each monitoring period although the peak levels did fluctuate. We hypothesize these neutron doses are due to the Californium sources in the time-of-flight facility. This Californium facility has since been moved to a more shielded location.

The calibration factors used to interpret the neutron response of all the TLDs are appropriate for the purely thermal neutron sources in the guide hall. The reported environmental results should not be used as a measure of the harder cosmic spectrum neutron dose.

The TLD monitoring program will continue with its present plan until all guide hall experimental stations are operational and doses are demonstrated to be acceptably low.

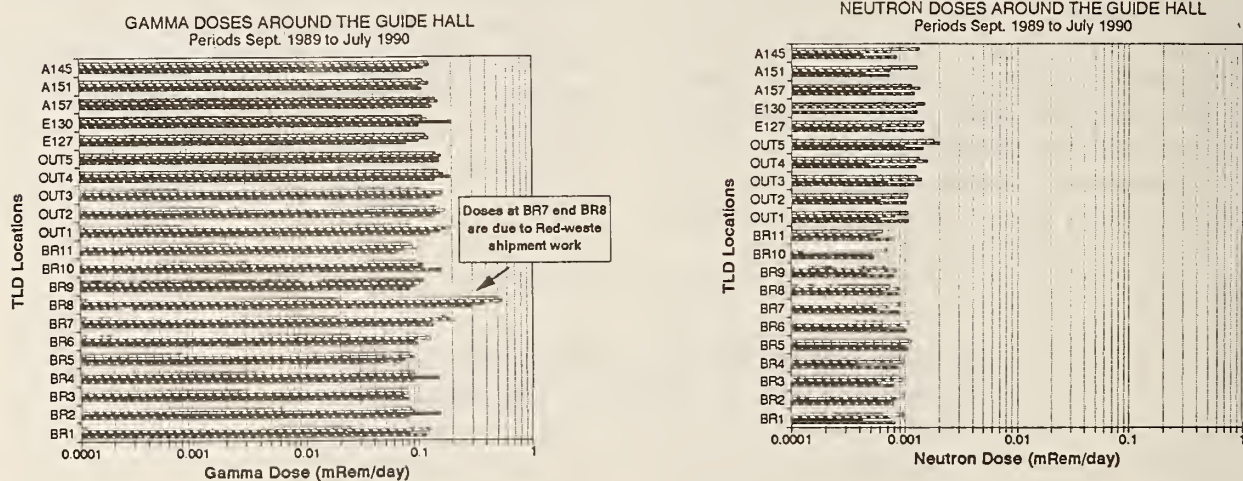


Figure 1. Results of the locations around the guide hall for the first four periods of data collection.

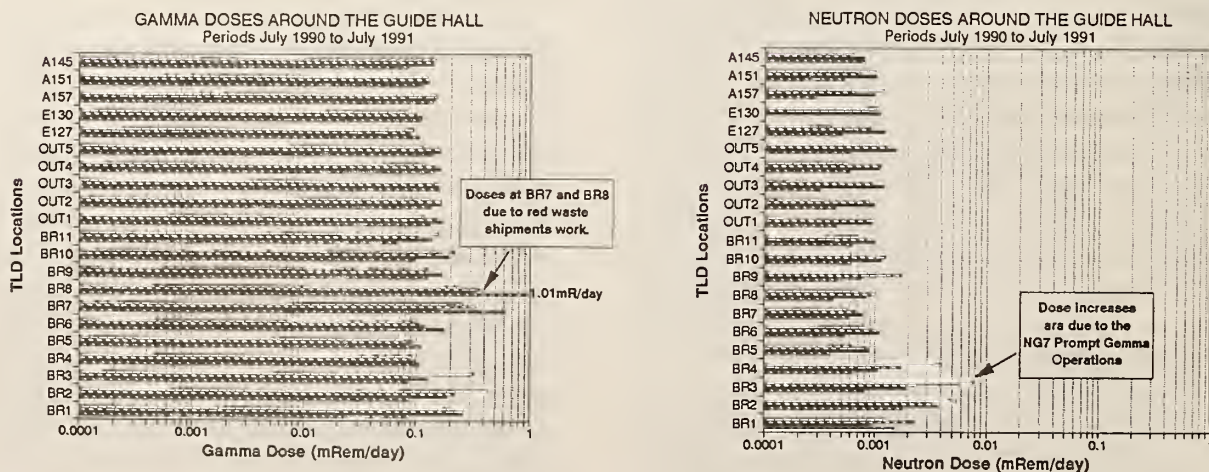
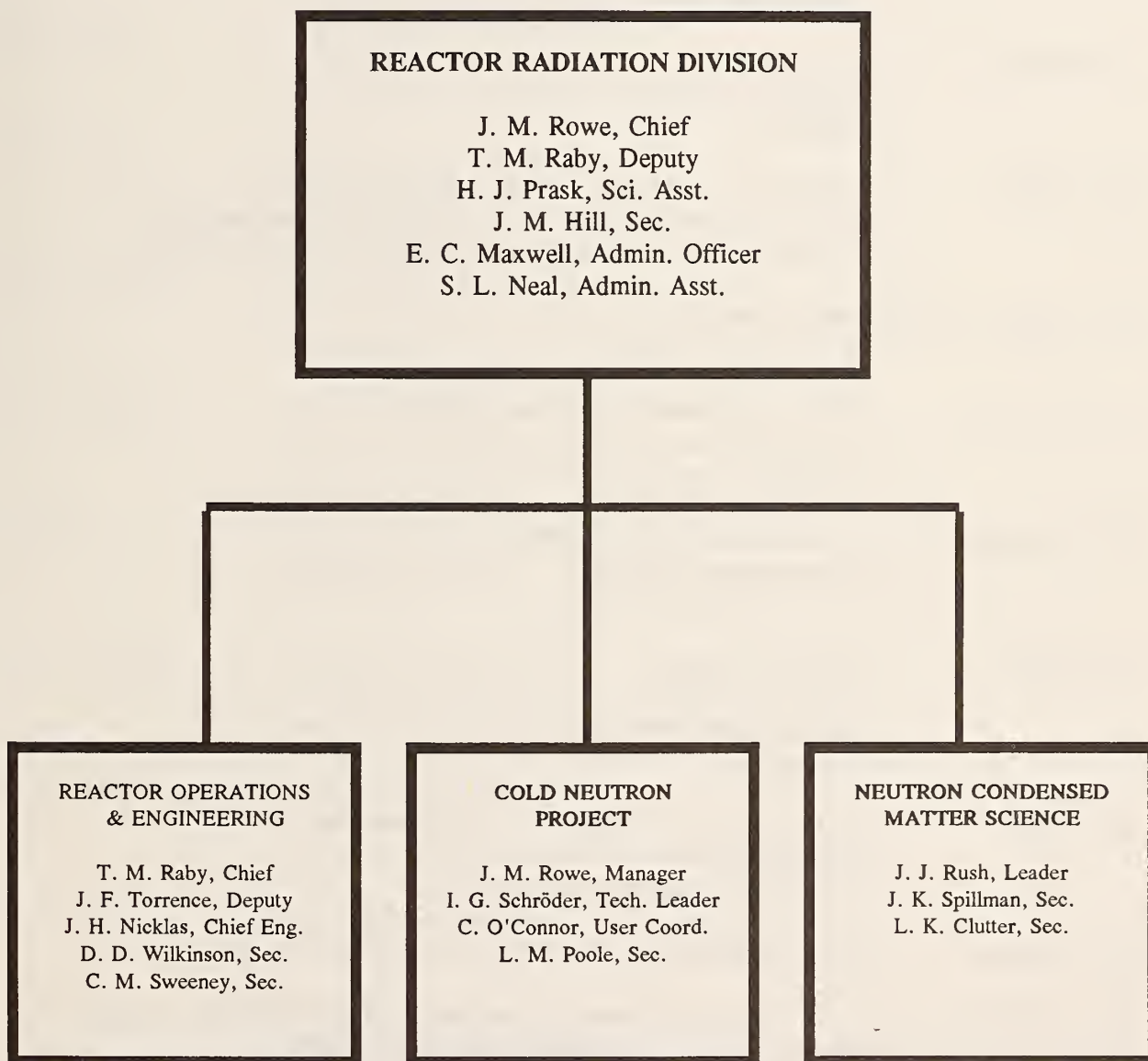


Figure 2. Results of the four periods from July 1990 to July 1991.

## G. PERSONNEL ROSTER



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